Applications of a Recycled-Flow Fourier Transform Nuclear Magnetic Resonance System: Molecular Weight Determination of Siloxane Polymers by ^{29}Si NMR

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ABSTRACT: Recycled-flow nuclear magnetic resonance methods are employed in the end-group analysis of six siloxane polymers. $\overline{\text{MW}}_n$ values ranging from 495 to 3773 are determined from quantitative ^{29}Si and ^{13}C NMR spectra. Experiment time and spectral quality are compared for quantitative NMR measurements obtained by static gated-decoupled measurements, use of Cr(acac)$_3$ as a relaxation reagent, and flow methods. Flow nuclear magnetic resonance is demonstrated to be superior to the use of relaxation reagents in leveling spin–lattice relaxation and minimizing the nuclear Overhauser effect; a factor of 3–5 improvement in analysis time and improved spectral resolution are reported. Finally, the general applicability of the method is demonstrated by applying quantitative flow NMR to the end-group analysis of water-soluble poly(ethylene glycols).

Application of nuclear magnetic resonance spectrometry (NMR) to the end-group analysis of linear polymers for the elucidation of a number-averaged molecular weight ($\overline{\text{MW}}_n$) is well established.[1-4] Unfortunately, spin-$^1/_2$ nuclei (including ^{13}C, ^{29}Si and ^{15}N) exhibit wide variations in spin–lattice relaxation times (T_1) and nuclear Overhauser effects (NOE) that necessitate a careful choice of spectral parameters to ensure quantitative conditions are maintained for all sample nuclei.[5,6] The two most common approaches to quantitative measurement of NMR spectra are (1) use of a gated-decoupled pulse sequence with delays between scans of 5–10 times the longest T_1 in the sample and (2) addition of a relaxation reagent such as chromium triacetylacetonate (Cr(acac)$_3$) which enhances nuclear–electronic relaxation and thus effectively levels T_1 values and suppresses the NOE.[7,8] In the absence of efficient relaxation processes, gated-decoupled measurements often require prohibitively excessive experiment times. Potential disadvantages of relaxation reagents include sample contamination, chemical reaction with the sample, perturbation of chemical shift and spectral line shape, and limited sample solubility.[9] In addition, even with the effective reduction of T_1's by the relaxation reagent, delays of a few seconds are generally required to ensure suppression of the NOE in samples with strong dipole–dipole interactions.[10]

Recently, we described a recycled-flow NMR technique which permits effecient quantitative measurement of samples with slowly relaxing nuclei.[11-13] Provided the residence time in a premagnetization region exceeds 5 times T_1 of the longest relaxing nucleus ($T_{1\max}$), quantitative conditions are achieved because saturation and NOE buildup are minimized through the constant efflux of excited nuclei from the observation region. Advantages of the recycled-flow measurement method include efficient data acquisition (with experiment recycle time (T_c) approaching the data acquisition time (T_a)) and an independence from sample-related spectral, solubility, and reactivity problems which restrict the use of relaxation reagents. However, because in essence the flow experiment trades sample volume for experiment time, a minimum of several milliliters of sample is required for the analysis. Several chemical applications including polymer and fuel analysis often are not constrained by this volume requirement and are ideal for routine flow NMR measurements. As demonstrated here in the end-group analysis of a variety of siloxane and poly(ethylene glycol) polymers, recycled-flow NMR compares favorably with either gated-decoupled or relaxation reagent techniques, often yielding substantial improvements in experiment time or spectral quality.

A qualitative understanding of the effects of a flowing system on the absorptive NMR signal can be obtained from an examination of eq 1 and 2. Flow system behavior

$$\frac{1}{T_{1\text{flow}}} = \frac{1}{T_{1\text{static}}} + \frac{1}{\tau} \tag{1}$$

$$\frac{1}{T_{2\text{flow}}} = \frac{1}{T_{2\text{static}}} + \frac{1}{\tau} \tag{2}$$

is most easily described as an effective decrease in both spin-lattice ($T_{1\text{flow}}$) and spin–spin ($T_{2\text{flow}}$) relaxation rates relative to static measurements, because of a decrease in the average lifetime of a sample nucleus, τ, in the observation region. As flow rate increases and τ decreases, the decrease in effective relaxation time is manifested through an increase in both signal intensity and spectral line width. In practice, signal enhancement in the flow measurement is achieved not only by an increased data acquisition rate compared to the static measurements but also because a premagnetization volume is inserted prior to the observation region to ensure preequilibration of all sample nuclei. The degradation in spectral line width inferred from eq 2 is attributed to the constant efflux of excited nuclei from the observation cell during data acquisition and is most pronounced at high flow rates when small observation volumes are employed. However, experimental conditions usually are established such that flow system contributions to the overall line shape are insignificant except for very high resolution measurements.

In the present work, six linear siloxane polymers, sold commercially as gas chromatography stationary phases, are utilized in a comparison of the three methods described above for quantitative NMR measurement. Both ^{29}Si NMR and ^{13}C NMR yield $\overline{\text{MW}}_n$ values for each siloxane from end-group analysis. ^{29}Si NMR has proven superior to ^{13}C NMR in the analysis of siloxanes because of the simplicity in distinguishing end and middle groups, as well as tertiary and quaternary branching, and polymer blends.[14,15] Unfortunately, inefficient spin–lattice relaxation ($T_1 > 25$ s) and a deleterious negative NOE contribute to the difficulty of quantitative ^{29}Si NMR measurement.[16] Previous $\overline{\text{MW}}_n$ studies of siloxane polymers have required the use of 0.02–0.1 M Cr(acac)$_3$ to achieve satisfactory spectral signal-to-noise (S/N) for quantitative measurement within reasonable time periods. In the present study, quantitative flow measurements compare favorably with

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Table I
NOE and T_1 Data for Polymeric Siloxanes Analyzed by Quantitative NMR

			^{29}Si T_1, s		^{29}Si η		
name	repeating unit structure	sample	end	middle	end	middle	^{13}C $T_{1\max}$, s
SF96	dimethylsiloxy	1:1 $CDCl_3$	60	53	−0.7	−1.4	7.6
		0.05 M $Cr(acac)_3$	1.1	1.0			
		0.1 M $Cr(acac)_3$	I[a]	I			
OV101	dimethylsiloxy	1:1 $CDCl_3$	35	46	−0.2	−1.4	9.8
		0.05 M $Cr(acac)_3$	1.9	1.5			
		0.1 M $Cr(acac)_3$	1.0	0.7			
FS1296	50% (trifluoropropyl)methylsiloxy	1:1 $CDCl_3$	38	16	−1.0	−2.4	5.3
		0.05 M $Cr(acac)_3$	1.1	1.2	0.0	−0.11	
		0.1 M $Cr(acac)_3$	I	I			
DC550	phenylmethyl- and dimethylsiloxy blend	1:1 $CDCl_3$	53, 49	47, 34	−1.1	−1.7	8.6
		0.05 M $Cr(acac)_3$	0.8, 0.8	0.7, 0.7			
		0.1 M $Cr(acac)_3$	0.4, 0.4	0.3, 0.3			
DC710	50% phenylmethylsiloxy	1:1 $CDCl_3$	50	23	−1.2	−1.9	6.8
		0.05 M $Cr(acac)_3$	0.8	0.7	0.0	0.0	
		0.1 M $Cr(acac)_3$	0.3	0.3			
OV17	50% phenylmethylsiloxy	1:1 $CDCl_3$	59	28	−1.0	−1.9	5.6
		0.05 M $Cr(acac)_3$	0.7	0.8			
		0.1 M $Cr(acac)_3$	0.5	0.4			

[a] $Cr(acac)_3$ is insoluble in 1:1 siloxane–$CDCl_3$ mixture.

the use of $Cr(acac)_3$, as superior spectral quality and decreased experiment times are obtained.

Further evidence of the general applicability of the quantitative flow-NMR procedure is exhibited through the quantitative analyses of two water-soluble poly(ethylene glycols) (PEG). The insolubility of $Cr(acac)_3$ in aqueous environments precludes a comparison with flow NMR, although flow NMR is demonstrated to be more efficient than the gated-decoupled procedure, even for samples with efficient spin–lattice relaxation ($T_1 \sim 1$ s).

Experimental Section

The schematic diagram in Figure 1 depicts the major components of the recycled flow system. Open-ended 5-mm NMR tubing in the observation region is connected at the inlet beneath a commercial NMR probe to a premagnetization volume consisting of 5–25 mL of coiled Teflon or glass tubing. At both the entrance and exit, this unit is attached by Teflon or nylon Swagelok fittings to $^1/_{16}$-in. Teflon tubing that leads to a peristaltic pump. A small reservoir beside the pump collects the sample for recycling. Total system volume varies depending upon the sample T_1 (as T_1 increases, sample volume should increase to maintain optimum data sampling) but typically ranges from 5 to 30 mL. If the amount of sample is limited, smaller premagnetization volumes and slower flow rates may be used. Recent efforts to decrease the flow system sample volume by replacing the premagnetization volume (5–30 mL) with an immobilized free radical substrate (<1 mL) have been successful.[12,17]

The siloxane samples used in the study are listed in Table I. Relevant ^{29}Si NMR data for the siloxanes, mixed 1:1 with $CDCl_3$, and with 0.05 and 0.1 M $Cr(acac)_3$ added, are included. The PEGs, obtained from Sigma, were dissolved in D_2O. T_1 values were obtained by using an inversion–recovery pulse sequence. NOE data were obtained from a comparison of decoupled and gated-decoupled spectra. Quantitative ^{29}Si NMR spectra were acquired at 59.6158 MHz by using a gated proton decoupled pulse sequence with 16K data collected over a ±4000-Hz bandwidth, with tetramethylsilane (Me_4Si) employed as an external chemical shift standard. ^{13}C NMR measurements for both the siloxanes and PEGs were acquired at 75.4097 MHz by using a gated proton decoupled pulse sequence with 16K data collected over a spectral width of ±8000 Hz. Experiment recycle time and the number of scans were varied to illustrate both quantitative and nonquantitative behavior and to compare spectral signal-to-noise (S/N) for the three quantitative measurement modes. Specific flow and spectral parameters for each polymer sample are included in Tables II–IV and the figure captions.

Quantitative measurement of middle and end groups in the spectra was determined by peak integration. To ensure accuracy and reproducibility in the peak areas, a minimum of 8–10 data points was required to adequately define the individual line shapes. Depending upon the natural line width of the resonance, application of a 0.5–3.0-Hz line-broadening function and a single zero-fill was sufficient for this purpose. For each resonance, a minimum spectral S/N of 15–20 was required to minimize errors in the measurement. Even with these precautions, integration errors of 2–5% are expected due to a combination of uncertainties in NMR data acquisition and processing.[5-7]

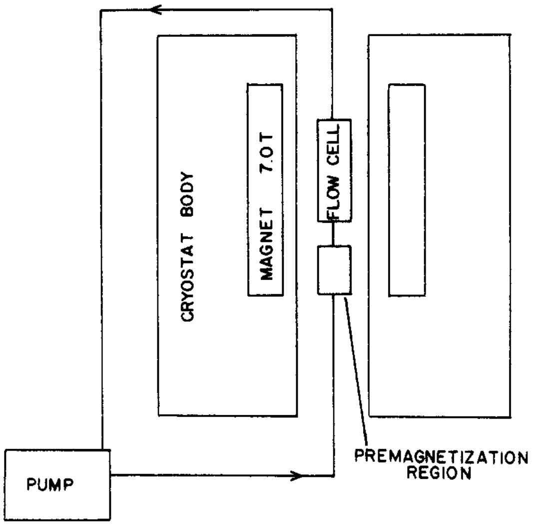

Figure 1. Schematic representation of the recycled-flow NMR instrumentation.

^{29}Si NMR data simplify the calculation of $\overline{MW}_n$ for the linear siloxanes because of the 20–40 ppm chemical shift difference between end and middle groups and the simplicity of spectral features associated with the siloxane backbone. Equation 3 expresses the average chain length, n, for linear siloxanes, with a and b equal to the integrated areas of the middle and end groups, respectively.

$$n = 2a/b \tag{3}$$

The actual calculation of $\overline{MW}_n$ requires a knowledge of end- and middle-group chemical structure, the determination of which is facilitated by ^{13}C NMR. A further advantage of ^{29}Si NMR is that polymer branching or copolymer blends are easily recognized through the presence of unique resonances or splitting patterns.[14] ^{13}C NMR also can be used to determine the average chain length if one knows the repeating unit structure within the polymer. With this information, it is possible to independently confirm both polymer structure and molecular weight if the average number of carbons per repeating unit can be determined. Equations 4–6 yield the average chain length for dimethylsiloxane,

Table II
Comparison Data for ^{29}Si NMR End-Group Analysis of Silicone DC710[a]

expt no.	measurement mode	scans	tot time, min	T_p,[b] s	$5T_{1max}$[c] or τ, s	T_c, s	quantitative conditions	ratio[d]
1	static	200	7.6		250	2.3	no	10.7
2	static	40	40.2		250	60.3	no	9.4
3	static 0.05 M Cr(acac)$_3$	672	14.7		4.0	1.3	no	8.4
4	flow, 13 mL/min	1500	12.7	115	1.15	0.5	no	9.0
5	flow, 13 mL/min	750	12.8	115	1.15	1.0	no	8.2
6	flow, 13 mL/min	200	8.4	115	1.15	2.5	no	7.6
7	static 0.05 M Cr(acac)$_3$	672	44.5		4.0	4.0	yes	7.4
8	flow, 8 mL/min	672	20.4	225	1.9	1.9	yes	7.3
9	flow, 5 mL/min	500	29.4	360	3.0	3.5	yes	7.3
10	flow, 5 mL/min	200	16.7	360	3.0	5.0	yes	7.4

[a] A 250-μL observation cell with a 30-mL premagnetization volume was used. [b] With T_{1max} of 50 s, a 250-s premagnetization time is required for quantitative analysis. [c] Quantitative conditions require $T_c > 5T_{1max}$ (static) or $T_c > \tau$ (flow). [d] Ratio = (integrated middle-group intensity)/(integrated end-group intensity).

Table III
Spectral S/N and End-Group Data for SF96 and FS1265 Siloxane Polymers

sample	expt no.	measurement mode	scans	T_c, s	tot time, min	S/N end	S/N middle	ratio
SF96	1	no Cr(acac)$_3$	820	10.0	151	4	50	29.2
	2	no Cr(acac)$_3$	32	301.0	160	5	83	24.8[a]
	3	0.05 M Cr(acac)$_3$	820	3.0	41	11	353	30.8
	4	0.05 M Cr(acac)$_3$	820	10.0	151	22	370	24.8[a]
	5	flow, 8 mL/min	820	1.0	14	21	375	29.5
	6	flow, 8 mL/min	820	4.0	55	32	478	24.4[a]
FS1265	7	no Cr(acac)$_3$	400	10.8	72	3	18	19.9
	8	no Cr(acac)$_3$	100	225.8	376	8	24	10.2[a]
	9	0.05 M Cr(acac)$_3$	1000	1.3	21	11	33	8.0
	10	0.05 M Cr(acac)$_3$	188	6.0	21	6	24	10.7[a]
	11	flow, 12 mL/min	1000	1.0	17	13	35	9.6
	12	flow, 12 mL/min	1000	1.3	21	15	39	10.2[a]

[a] Quantitative measurement.

Table IV
Comparison Resolution Data for Quantitative Measurement Modes

	resolution,[a] Hz static spinning	0.05 M Cr(acac) spinning	flow[b]
SF96	1.32	2.19	1.44
OV101		1.17	0.90
FS1265	3.01	5.82	2.64[c]
DC550		3.57	1.39
DC710		3.36	1.56
OV17		2.66	1.48

[a] Measured as full width at half-height from the trimethylsiloxy end group for a wide-band proton-decoupled experiment. A 0.5-Hz line-broadening function was applied to each transient. [b] Flow rates varied from 8 to 12 mL/min. [c] Long-range Si-F coupling contributes to the line broadening.

50% (trifluoropropyl)methylsiloxane, and 50% phenylmethylsiloxane if trimethylsiloxy end capping is assumed.

$$n = 3a/b \tag{4}$$

$$n = 3a/2b \tag{5}$$

$$n = 6a/7b \tag{6}$$

Results and Discussion

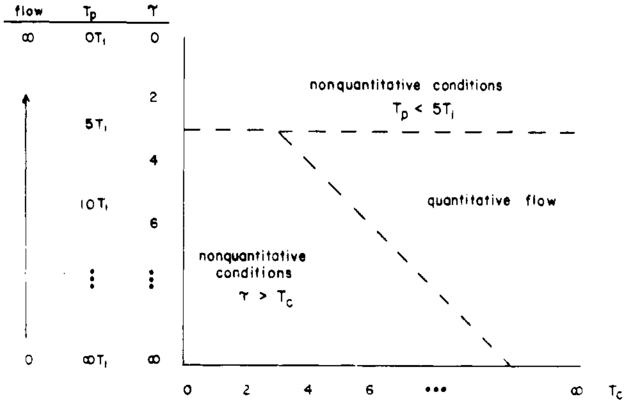

Figure 2. The two conditions for quantitative flow, $T_c > \tau$ and $T_p > 5T_1$, are demonstrated graphically as a function of flow rate and recycle time.

Quantitative Flow NMR. The graph in Figure 2 describes the two basic requirements to ensure the integrity of the quantitative flow NMR measurement: (1) all sample nuclei must be completely premagnetized prior to observation; (2) once excited, nuclei must be removed from the observation region between scans to prevent saturation or buildup of NOE. Provided sufficient sample is available, premagneitzation occurs as the sample flows through a glass coil attached directly below the probe in the magnetic field. Assuming ideal flow behavior, one can estimate the lifetime in the premagnetization region (T_p) from the rate (f) and premagnetization volume (V_p). The maximum flow rate (f_{max}) allowed for quantitative measurement is calculated from eq 7. In practice, some mixing occurs in the

$$f_{max} = V_p/T_p = V_p/5T_{1max} \tag{7}$$

premagnetization region because of nonideal flow characteristics, which may permit quantitative measurement with a somewhat smaller T_p (or larger f_{max}). To determine flow system design parameters, the maximum T_1 for the samples to be analyzed is estimated and all nuclei with shorter T_1s are assumed to be completed premagnetized.

For example, with V_p equal to 10 mL, a flow rate of 10 mL/min permits quantitative evaluation of all nuclei with $T_1 < 12$ s ($5T_{1\max} = 60$ s).

The experiment recycle time, T_c, must be in excess of the lifetime τ of a nucleus in the observation region. The minimum τ value is calculated as the NMR observation cell volume, V_c, divided by flow rate. However, because nonideal flow may occur in the observation cell, T_c is often set to greater than the τ value calculated from f and V_c. The problem is most severe when slower flow rates are required because of limited sample. Although, ideally, $T_c = T_a$ to achieve the most impressive savings in experiment time, this procedure usually is employed only in signal-enhancement measurements for which quantitative data are not required.[12]

As suggested by the T_1 and NOE data contained in Table I, quantitative analysis of ^{29}Si NMR data is not feasible when the conventional gated-decoupled technique is used because the large $T_{1\max}$ values for the siloxanes require a T_c of several hundred seconds. However, addition of Cr(acac)$_3$ effectively levels T_1 values to around 1 s, significantly improving the applicability of ^{29}Si NMR to polymer end-group analysis. It has been suggested that if middle- and end-group T_1's are essentially equivalent, then satisfying the requirement that $T_c = 5T_{1\max}$ is unnecessary, and flip angles and delays may be chosen to maximize signal while still retaining quantitative behavior.[14] Unfortunately, although this approach is occasionally successful, nonquantitative conditions often will occur. As the data in Table I indicate, not only is it possible that T_1s will be insufficiently leveled as is observed for OV101 siloxane polymer but the potential for incomplete quenching of the NOE in samples with strong dipole–dipole interactions exists, as is observed for the FS1296 sample. Unless a complete evaluation of sample T_1 and NOE values is performed prior to end-group analysis, a gated-decoupled measurement with a T_c of several seconds is essential to ensure quantitative behavior when Cr(acac)$_3$ is added to the sample.

Comparison data for the 50% phenylmethylsiloxane polymer, DC710, in Table II and Figure 3a suggest the necessary conditions for quantitative behavior in the three experiment modes. As expected, the static measurement with Cr(acac)$_3$ requires excessive experiment times to obtain the quantitative middle to end group ratio of 7.4. Smaller recycle times yield much higher ratios because of the more efficient middle-group T_1 relaxation (experiments 1 and 2 in Table II). Addition of 0.05 M Cr(acac)$_3$ significantly reduces the recycle time, although with $T_c < 5T_1$, a quantitative ratio is not achieved (experiment 3).

Several flow measurements were performed with DC710 to evaluate the requirements for quantitative behavior. In experiments 4–6, a flow rate of 13 mL/min permits equilibration for only $2.3T_1$ in the premagnetization volume, insufficient for premagnetization of end-group nuclei; hence, the middle to end group ratio is too large. However, as T_c increases from experiment 4 to 6, saturation effects decrease and the measurement becomes increasingly quantitative. The three quantitative flow experiments, experiments 8–10, demonstrate a leveling in the middle to end group ratio as the two quantitative flow requirements are met. Examination of results of experiments 7 and 8 affords a direct comparison of experiment times for the Cr(acac)$_3$ and flow measurement. For the same number of scans, the improvement in measurement time as determined by the ratio of recycle times establishes a factor of 2.1 improvement for the flow experiment despite the less than optimum flow rate.

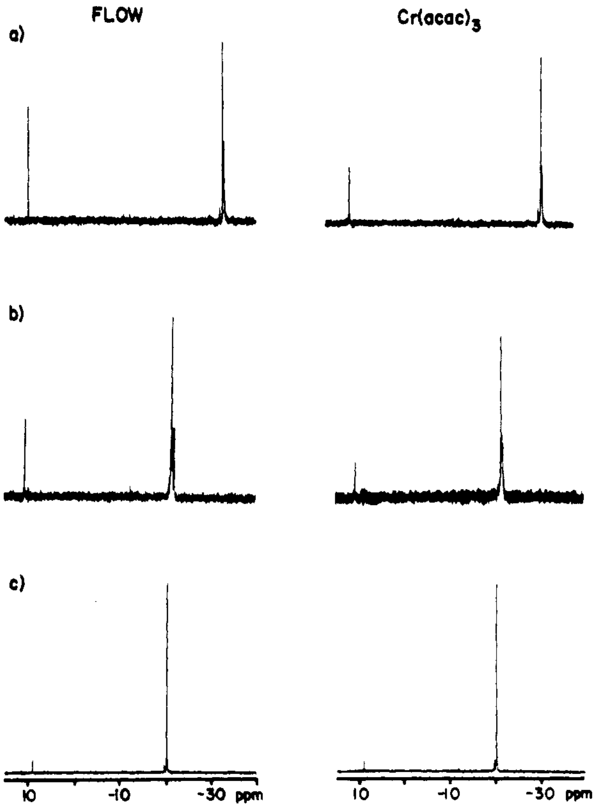

Figure 3. ^{29}Si NMR spectra of three linear siloxanes are compared for flow and Cr(acac)$_3$ measurement. The simplicity of end-group analysis by ^{29}Si NMR is facilitated by the separation of middle and end groups. (a) Spectra of DC710 from experiments 7 and 8 in Table II. (b) Spectra of FS1265 from experiments 10 and 12 in Table III. (c) Spectra of SF96 from experiments 4 and 6 in Table III.

Table III and Figure 3b,c provide a further evaluation of the quantitative measurement modes. For both SF96 and FS1265 polymers, the flow rate chosen permits premagnetization times in excess of $4T_{1\max}$. Recycle times of 4.0 and 1.3 s exceed τ values of 1.9 and 1.25 at the flow rates of 8 and 12 mL/min, respectively, and complete the requirements for quantitative flow. These recycle times are substantially smaller than those required for static system measurements, which require $T_c = 5T_{1\max}$.

If saturation effects are the predominant contribution to nonquantitative behavior in ^{29}Si NMR, the most slowly relaxing nuclei resonances (the end group in the six polymers presented here with the exception of OV101) are suppressed relative to other resonances. For example, as observed with the DC710 and SF96 data in Tables II and III, the middle to end group ratio usually decreases to a constant value as the recycle time is increased. However, both the static Cr(acac)$_3$ and flow NMR FS1265 experiments yield a ratio that increases to a constant value as recycle time increases. This behavior is attributed to a strong negative NOE, which acts to decrease the middle-group signal intensity. As seen in Table I, FS1265 exhibits the strongest NOE and most efficient middle-group relaxation of the polymers. Levy demonstrated that, even with addition of Cr(acac)$_3$, NOE may not be fully suppressed in larger molecules with strong dipole–dipole relaxation, which can compete with electronic–nuclear relaxation.[16] The incomplete suppression of NOE in the FS1265 sample with 0.05 M Cr(acac)$_3$ provides confirmation of this observation (Table I). These data provide further evidence that a T_c of several seconds is essential if relaxation reagents are used for quantitative analysis. In contrast, the flow measurement recycle time is based

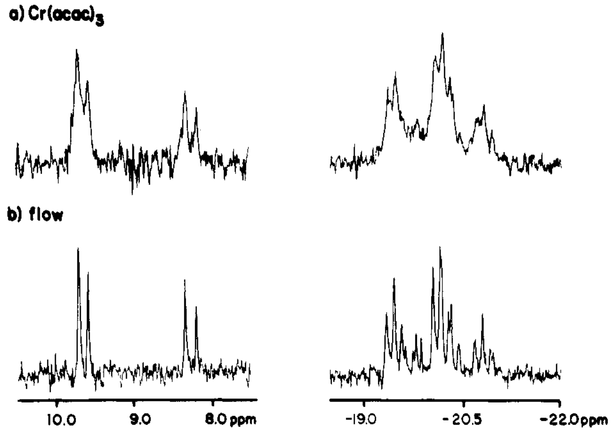

Figure 4. Spectra of the end- and middle-group regions of the DC550 phenylmethylsiloxane copolymer blend demonstrate the reduced spectral quality derived from (a) the 0.05 M Cr(acac)$_3$ sample compared to (b) the flow measurement.

strictly upon the ability to remove excited sample from the observation cell and is independent of chemical environment.

As seen from Table I, when the concentration of Cr(acac)$_3$ is increased in a sample, T_1 values decrease and permit more efficient data acquisition. Unfortunately, deleterious side effects of increased Cr(AcAc)$_3$ concentrations include an increase in NMR line widths and degradation of spectral features; above a concentration of 0.05 M Cr(acac)$_3$, spectral quality becomes unacceptable. Table IV compares line width data for the trimethylsiloxy end group from each siloxane for the three experiment modes. As expected, spectral resolution for the static spinning and flow measurements is similar while the line widths broaden significantly for the samples with 0.05 M Cr(acac)$_3$. The loss of spectral features essential to the analysis of siloxane polymer structure suggests that Cr(acac)$_3$ should not be used except for quantitative measurements which do not require high spectral resolution. Figure 4 presents expanded end- and middle-group spectral regions for the DC550 phenylmethylsiloxane polymer blend that clearly illustrate the superior spectral quality achieved with flow measurements.

For simplicity, a ratio of recycle times is used to compare the efficiency of various measurement modes. A more accurate assessment would require a correction for the loss in spectral S/N associated with line-broadening effects for flow and Cr(acac)$_3$ measurement. Although losses in resolution for the flow experiment are minimal (Table IV), increasing the concentration of Cr(acac)$_3$ in the sample adversely affects the line width, and ultimately S/N. Optimization of spectral S/N as a function of Cr(acac)$_3$ concentration would require evaluation of both $T_{1\max}$ and line width. Comparison of the S/N data in Table III indicates that superior S/N is achieved with the quantitative flow measurement relative to the static Cr(acac)$_3$ measurement. For example, comparison of experiments 4 and 6 in Table III shows that flow experiment middle-group S/N exceeds the static Cr(acac)$_3$ measurement by 29% despite an equivalent number of scans.

Table V
Comparison of Flow and Static Quantitative Measurement Parameters for PEG 600 and 1450 Samples[a]

sample	measurement mode	scans	T_c, s	tot time, min	ratio
PEG 600	spinning	144	1.5	6.1	15.7
	spinning	336	8.5	47.6	12.2[b]
	flow, 25 mL/min	500	0.4	4.2	16.5
	flow, 25 mL/min	500	1.0	8.4	13.8
	flow, 25 mL/min	336	1.5	8.4	12.1[b]
	flow, 25 mL/min	256	2.0	8.4	11.5[b]
PEG 1450	spinning	308	1.5	10.0	43.9
	flow, 25 mL/min	468	1.0	10.0	35.8
	flow, 25 mL/min	308	1.5	10.0	32.2[b]

[a] $T_{1\max}$ for the PEGs was 1.6 s. [b] Quantitative measurement.

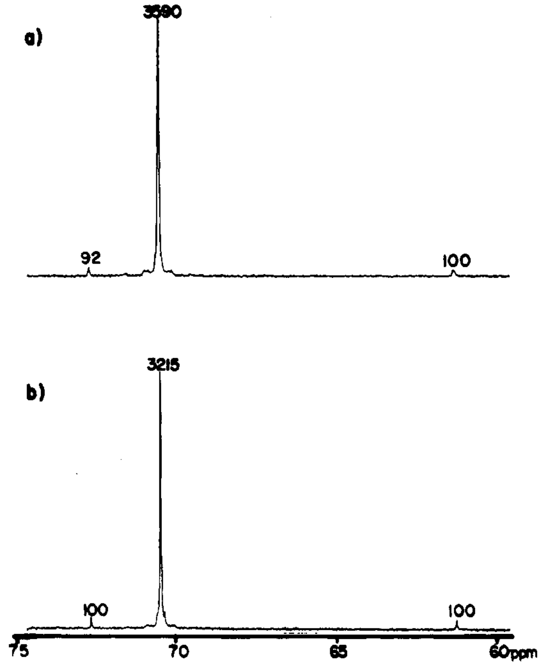

Figure 5. ^{13}C NMR spectra of PEG 1450 obtained in 10.0 min with 308 scans acquired and T_c = 1.5 s for (a) gated-decoupled and (b) flow measurements. The integrated peak areas indicate nonquantitative behavior occurs in the static measurement.

A further disadvantage of Cr(acac)$_3$ is its insolubility in aqueous environments. Although several water-soluble relaxation reagents have been proposed,[18] they suffer from the negative side effects attributed to Cr(acac)$_3$. Table V contains static and flow quantitative ^{13}C data for water-soluble PEG 600 and PEG 1450. Despite $T_{1\max}$ values of 1.6 s for the PEG end groups which permit efficient quantitative data acquisition without relaxation reagents, a factor of 4 improvement in experiment time is still obtained by flow NMR. Calculations based upon the integrated peak areas in Figure 5 demonstrate that an injudicious choice of T_c for the static measurement of the PEG 1450 yields a 25% error in $\overline{MW}_n$, despite the efficient dipole–dipole relaxation.

To this point, only ^{29}Si NMR data have been considered in the evaluation of silicone polymer $\overline{MW}_n$ values. However, ^{13}C NMR may be utilized in an analogous manner and offers several advantages compared to the use of ^{29}Si NMR. As seen in Table I, the order-of-magnitude decreases in $T_{1\max}$ and a positive NOE suggest that data acquisition should be more efficient and reliable. However, because addition of Cr(acac)$_3$ or use of flow NMR for the quantitative measurement effectively levels both the T_1 and NOE values for both nuclei, only the relative sensitivity of ^{29}Si to ^{13}C, a factor of 2.1, is relevant and indicates that ^{29}Si NMR should be more efficient. The inability of ^{13}C NMR to distinguish siloxane middle and end groups has been suggested as a limitation of the technique.[14,15] However, that work was performed at lower magnetic fields; at a ^{13}C NMR resonance frequency of 75 MHz there was no difficulty in isolating the terminal trimethylsiloxy group in each sample, thus permitting $\overline{MW}_n$ to be obtained by ^{13}C NMR.

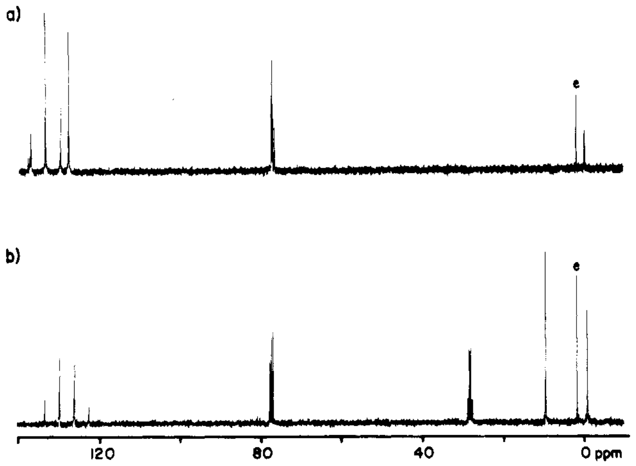

Figure 6. Quantitative ^{13}C spectra of (a) OV17 and (b) FS1265 siloxane polymers in $CDCl_3$, with "e" designating the end-group resonance.

Table VI
Summary of $\overline{MW}_n$ Data for Siloxanes and PEGs[a]

sample	n			$\overline{MW}_n$	expt time ratio[b]
	^{29}Si flow	^{29}Si static	^{13}C		
SF96	48.8	49.6	48.0	3773	2.7
OV101	4.5		4.7	495	6.2
FS1265	20.4	21.6	18.2	3344	4.6
DC550	20.4	19.8	20.4	2417	2.7
DC710	14.6	14.8	15.0	2148	3.0
OV17	19.6	20.4	19.2	2838	2.7

sample	^{13}C flow	^{13}C static	$\overline{MW}_n$	expt time ratio[b]
PEG 600	11.5	12.1	596	5.7
PEG 1450	32.1	32.2	1502	

[a] $\overline{MW}_n$ value uses n from ^{29}Si flow data and includes trimethylsiloxy end groups. [b] Ratio of $[T_c(\text{flow})]/[T_c(\text{static})]$ for flow and 0.05 M $Cr(acac)_3$ measurements.

Although ^{13}C NMR responances of the dimethylsiloxanes are easily assigned, more complicated polymer functional groups increase the complexity of ^{13}C NMR spectral assignment. The quantitative ^{13}C NMR spectra of OV17, a 50% phenylmethylsiloxane polymer, and FS1265, a 50% (trifluoropropyl)methylsiloxane polymer are presented in Figure 6. In each case, an average number of middle-group carbons per siloxyl group is determined, based upon prior knowledge of the polymer structure. The difference in integrated peak areas and line widths facilitates the selection of the end-group resonance and permits a calculation of n from eq 5 and 6.

Despite the ability to determine functional group information from ^{13}C NMR data, the ^{29}Si NMR spectrum is considerably more valuable in determining the presence of copolymer blends or branching. Figure 7 contains the ^{29}Si NMR and ^{13}C NMR spectra of the DC550 polymer; whereas the ^{13}C NMR spectrum provides evidence of a phenyl ring and methyl groups, only a second methyl group distinguishes it from the ^{13}C NMR spectrum of the 50% phenylmethylsiloxane polymer presented in Figure 6a. The quantitative ^{29}Si NMR spectrum, however, immediately suggests a copolymer blend of phenylmethylsiloxy and dimethylsiloxy repeating units in a 1.0:0.7 ratio.

Table VI summarizes the results for the six siloxanes, with n determined by ^{29}Si NMR flow and $Cr(acac)_3$ methods and by ^{13}C NMR. The $\overline{MW}_n$ value for each siloxane is calculated from the ^{29}Si NMR flow data. $\overline{MW}_n$ data from ^{13}C NMR flow and static experiments are also included. The agreement between ^{29}Si NMR and ^{13}C NMR data for the siloxanes is 1.0%, within the practical error limits associated with data acquisition and processing. Comparison of flow and $Cr(acac)_3$ recycle times for the ^{29}Si NMR data suggests a factor of 3–5 time savings is possible with flow measurements. This fact, coupled with improved spectral quality compared to $Cr(acac)_3$, suggests the value of flow NMR for quantitative evaluation in non-sample-limited measurements.

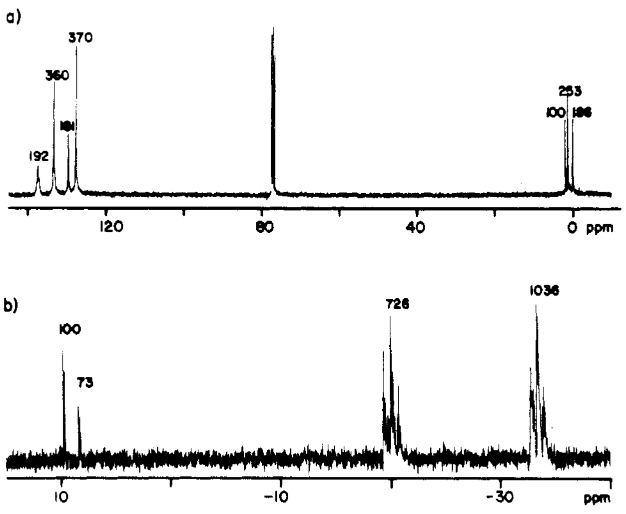

Figure 7. Quantitative (a) ^{13}C NMR and (b) ^{29}Si NMR flow spectra of DC550, a phenylmethylsiloxane polymer blend. Integrated peak areas are included and suggest a 1.0:0.7 ratio of phenylmethylsiloxy and dimethylsiloxy units. Peak assignments (from intensity data) include the following: (a) 100, trimethyl end group, 186, methyl group in phenylmethylsiloxy unit; 253, methyl group in dimethylsiloxy units; (b) 1036, siloxane resonance in phenylmethylsiloxy unit; 726, siloxane resonance in dimethylsiloxy unit.

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