Viscosity–Molecular Weight Correlations of Disiloxanols by ^{29}Si Fourier Transform Nuclear Magnetic Resonance

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ABSTRACT: ^{29}Si Fourier Transform NMR is used to measure the average degree of polymerization ($\overline{DP}$) of α,ω-dihydroxypolydimethylsiloxane fluid mixtures, $HO[(CH_3)_2SiO]_{\bar{n}}H$, where $\bar{n}$ = 6–80. A plot of $\overline{DP}$ vs. bulk viscosity gives a linear correlation, $\overline{DP} = \eta_{25°}(cs) - 26$. This disiloxanol $\overline{DP}$ viscosity correlation is compared to a similar correlation from gel permeation chromatography studies.

In recent studies of disiloxanol polymerizations, we needed a fast and accurate method to determine the average degree of polymerization of α,ω-dihydroxypolydimethylsiloxane fluid mixtures, 1, where $\bar{n}$ = 6–100. Since we intended to apply this method during the course of reactions, we preferred that the determination not entail derivatization of the fluids.

$HO[(CH_3)_2SiO]_{\bar{n}}H$ **1** $CH_3[(CH_3)_2SiO]_nSi(CH_3)_3$ **2**

The most convenient method of following changes in the average degree of polymerization ($\overline{DP}$) appeared to be measurement of the bulk viscosity of the fluid. Equation 1 relates the bulk viscosity or melt viscosity, η, of a polymer to the molecular weight:

$$\log \eta = A + C \log M \quad (1)$$

In eq 1, A and C are constants and M can be either the viscosity molecular weight, $\bar{M}_v$, or the weight-average molecular weight, $\bar{M}_w$.[1]

Lee, Polmanteer, and King[2] found a bulk viscosity–molecular weight correlation in agreement with eq 1 for hydroxy-terminated polydimethylsiloxanes where $\bar{M}_w >$ 30 000. However, from the scant data available, it was not possible to construct a reliable viscosity–molecular weight curve for the low molecular weight disiloxanols.

Several groups have investigated the flow behavior of low molecular weight methyl-terminated polydimethylsiloxanes. Wilcock[3] and Hunter et al.[4] determined the bulk viscosities of ten monodispersed polysiloxanes, 2, where n = 1–9. These viscosities were also found to relate to molecular weight in agreement with eq 1. Because of the polar terminal groups in the disiloxanols, the bulk viscosities of these low molecular weight fluids were expected to differ markedly from those of their methyl-terminated analogues. To construct a viscosity–molecular weight profile, we needed an accurate method of determining the average molecular weights of disiloxanol mixtures.

Gel permeation chromatography (GPC) has been used extensively to measure the molecular weights of various polysiloxanes. However, inherent in the use of GPC to determine disiloxanol molecular weights is a considerable degree of uncertainty. To convert raw GPC data, which are based on a polystyrene calibration, to disiloxanol molecular weights requires the calculation of a Q factor ratio.[5] This ratio is obtained from the relative Q factors for polystyrene and polydimethylsiloxane. The Q factors in turn are calculated from the formula weights and estimated repeat lengths of the monomer unit for the two polymers. The calculation of Q factor ratios introduces considerable uncertainty into the molecular weight determination. More significant in this case are the uncertainties introduced by potential intermolecular association of the polar disiloxanol end groups, especially at low molecular weights. The issue is further complicated by the affinity of the hydroxy end groups for polar sites in the cross-linked polystyrene network of the GPC columns. All these uncertainties combine to erode confidence in the disiloxanol molecular weights as determined by GPC.

Nevertheless, since GPC was a powerful and widely accepted technique, and also one of the few techniques actually available, 12 disiloxanol samples were analyzed by GPC. A Q-factor ratio of 0.62 was used to convert molecular weights from the GPC calculations to equivalent dimethylsiloxane molecular weights. (See Experimental Section.) In addition, the bulk viscosities of the 12 fluids were measured at 25°C. Table I lists the bulk viscosities along the weight average and number average molecular weights, $\bar{M}_w$ and $\bar{M}_n$, corrected for a Q-factor ratio of 0.62.

The solid curve in Figure 1 shows the log–log plot of bulk viscosity with $\bar{M}_w$. The broken line is a similar plot of viscosity vs. molecular weight for the monodispersed methyl-terminated fluids as reported by Hunter et al.[4] The two curves show that at a given molecular weight the viscosity of the hydroxy-terminated fluid is considerably higher than that of the methyl-terminated fluid. Since the upward swing of the disiloxanol curve is more pronounced at low molecular weights, it would seem that the cause of this viscosity elevation is intermolecular hydrogen bonding.

Though we now had in hand a molecular weight–viscosity correlation, because of the uncertainties inherent in GPC analyses, which we discussed above, we were unsure of the accuracy of the molecular weight data. Consequently we investigated several alternate techniques for measuring the average molecular weight of a disiloxanol mixture. Titration of the siloxanol hydrogen with methyl magnesium iodide and measurement of the volume of methane generated gave irreproducible results, apparently due to contamination of the fluids with water, protic solvents, and nonfunctional cyclic siloxanes. Titration with Karl Fisher reagent[6] was expected to suffer from the same deficiencies encountered using the Grignard reagent. Several disiloxanol samples were analyzed by vapor phase osmometry (VPO); unfortunately, the results were erratic. We suspected that intermolecular association might be the cause of this behavior in the VPO experiments.

From the outset of this study we had assumed that an end-group analysis using nuclear magnetic resonance would provide a method of measuring the $\overline{DP}$ of these low molecular weight disiloxanols. (The use of NMR to determine sequence lengths in polymers is well established.[7]) If the nuclei in the terminal (A) and internal (B) segments of the fluids (Figure 2) could be resolved and integrated by NMR, then eq 2 could be used to derive the average degree

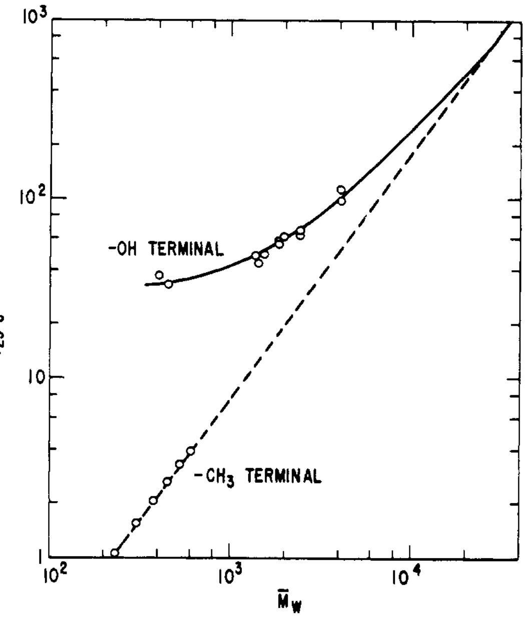


Figure 1. Plot of number average molecular weight vs. bulk viscosity for $-OH$ and $-CH_3$ terminated polydimethylsiloxanes.

Table I
Disiloxanol Bulk Viscosity Versus Chain Length ($\bar{n}$) by ^{29}Si NMR and GPC

		$\bar{n}$		
Sample No.	Bulk viscosity (250°), cs	By ^{29}Si NMR integration	By $M_{\overline{w}}$	By $M_{\overline{n}}$
1	34	7	10	8
2	37	7	9	7
3	44	24	27	18
4	48	22	30	22
5	49	23	34	19
6	57	37	40	22
7	58	34	40	26
8	61	34	43	28
9	63	36	53	34
10	67	47	51	24
11	99	83	89	56
12	111	80	88	54

of polymerization. To our surprise, a ^{13}C NMR spectrum of a typical fluid gave poor resolution of the methyl carbons. Also, both 60 and 100 MHz ^1H spectra did not resolve the different methyl hydrogens. Integration of the exchangeable hydroxyl hydrogens was considered too unreliable.

$$\overline{DP} = 2(B/A) + 2 \qquad (2)$$

Horn and Marsmann[8] had demonstrated that ^{29}Si NMR could resolve the terminal and internal silicon nuclei of low molecular weight disiloxanols. In our laboratory, a ^{29}Si NMR spectrum of a disiloxanol fluid using Fourier transform techniques and proton noise decoupling easily resolved the hydroxyl bearing terminal silicons from the internal dimethylsiloxane silicons. Figure 3 shows a spectrum of a fluid where $\bar{n}$ = 6. The spectrum was obtained on a 50 vol % solution of the disiloxanol mixture in 90:10 methylene chloride–acetone-d_6. The deuterated acetone was used as the internal field frequency lock. Approximately 0.1 mol of tris(acetylacetonato)chromium was added to reduce the long spin-lattice relaxation times (T_1's) on silicon and to suppress the negative nuclear Overhauser effect (NOE).[9] Tetramethylsilane (TMS) was added as internal standard.

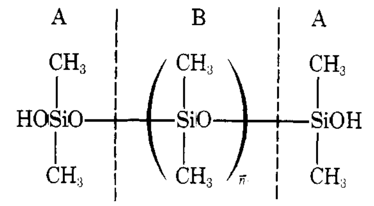


Figure 2. α,ω-Disiloxanol fluid mixture.

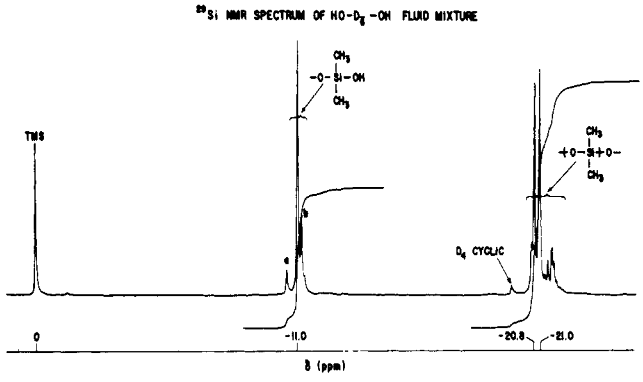


Figure 3. ^{29}Si NMR spectrum of $HO-[-Me_2SiO-]-_6H$.

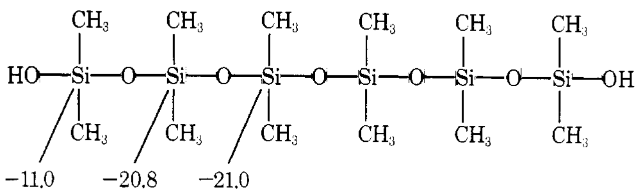


Figure 4. ^{29}Si NMR chemical shifts (ppm) of $HO[(CH_3)_2SiO]_6H$, ($HO-D_6-OH$).

The spectrum clearly shows the separation of the peaks in question. Moreover, because of the small number of species involved in this particular sample, namely the trimer, hexamer, and nonamer disiloxanols, resonances could be assigned to discrete disiloxanol species. The large low field resonance at −11.0 ppm was assigned to the hydroxyl-bearing silicons in $HO[(CH_3)_2SiO]_6H$ (abbreviated here as $HO-D_6-OH$). The two large upfield peaks at −20.8 and −21.0 ppm were assigned to the two sets of equivalent dimethylsiloxane silicons in the $HO-D_6-OH$ molecule (Figure 4).

Similarly, resonance "*b*" at −11.2 ppm in Figure 3 was assigned to the terminal silicons in $HO-D_3-OH$. The unique internal dimethylsiloxane silicon in $HO-D_3-OH$ was assigned to the low field shoulder of the −20.8 ppm resonance (−20.7 ppm). Low field resonance "*a*" along with the upfield cluster from −21.2 to −22.0 ppm were assigned to the respective silicons in $HO-D_9-OH$. A small amount of D_4 (octamethylcyclotetrasiloxane) could be detected in the mixture at −19.8 ppm.

When ^{29}Si NMR spectra of higher molecular weight fluids were obtained, the low field silanol silicon peaks coalesced into a single peak. Also, the internal dimethylsiloxane silicons usually coalesced into one resonance with some partially resolved fine structure. The entire series of disiloxanols was analyzed and their average DP's determined using this ^{29}Si NMR technique. The data were plotted against the bulk viscosity values previously measured (Figure 5). The plot shows a linear relationship of bulk viscosity with chain length over a range of 6 to 80 dimethylsiloxy units.

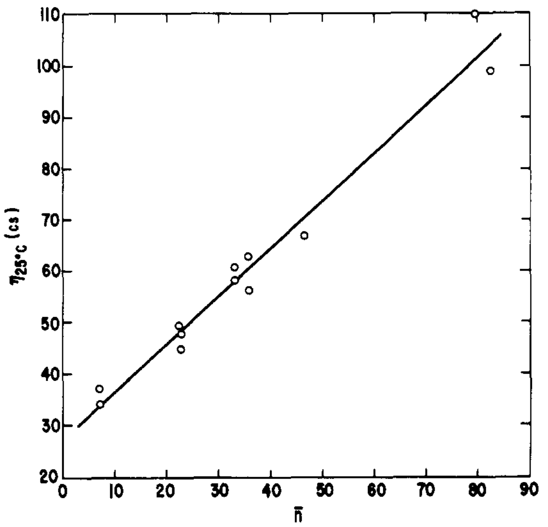
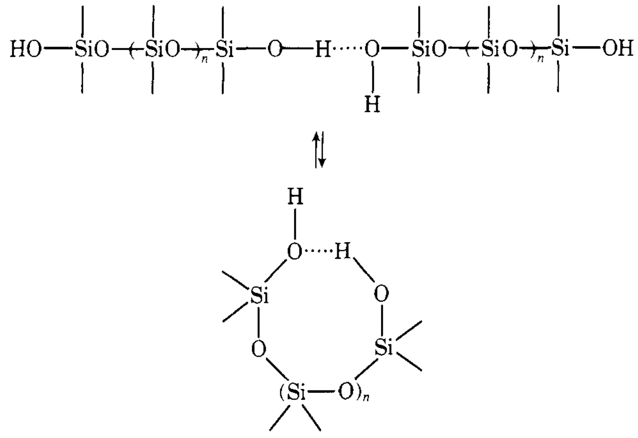


Figure 5. Plot of block length vs. bulk viscosity for -OH terminated polydimethylsiloxanes.

Scheme I
Intra- and Intermolecular Association of
α,ω-Disiloxanols



Since the $\overline{DP}$ measured by ^{29}Si NMR is directly convertible to $\bar{M}_n$, it is surprising to discover such a straightforward relationship. Classically, the flow of a polydispersed polymer fluid or melt correlates with $\bar{M}_w$, not with $\bar{M}_n$.[1] Furthermore, the $\bar{M}_w$ correlation is linear with viscosity only when plotted in a logarithmic fashion. Therefore, it is probably simply fortuitous that we find a nonlogarithmic linear relationship of disiloxanol viscosity with $\bar{M}_n$. Interestingly, the curve in Figure 5 is of unit slope. This finding provides a convenient rule-of-thumb to convert disiloxanol viscosity to $\overline{DP}$ (eq 3).

$$\overline{DP} = \eta_{25°}(\text{cs}) - 26 \qquad (3)$$

The shape of the curve in Figure 5 seems to contradict our previous explanation for the GPC-derived curve in Figure 1. We had explained the curvature of the log-log plot in Figure 1 as the result of increased intermolecular association at lower molecular weights, where the concentration of hydroxyl groups is higher. However, the ^{29}Si NMR data suggest that, though the viscosities of the disiloxanols are elevated compared to their methyl-terminated analogues, the effect is no more pronounced at lower molecular weights than at higher molecular weights.

Since the rate of change of disiloxanol viscosity does not vary with changes in hydroxyl concentration, another phenomenon must compete with intermolecular association, especially at lower molecular weights. We know that difunctional siloxanes have a propensity to form cyclic species;[11] it may be this tendency for intramolecular head-to-tail association which offsets the expected change in the viscosity profile at the low molecular weight end of the curve (Scheme I). Intramolecular association generates pseudo-cyclic species which act as diluents in the fluids. In equilibrium with these pseudo-cyclics are intermolecularly associated disiloxanols which tend to increase the viscosity. Since both modes of association are most likely at lower molecular weights, each mode can offset the effect of the other.

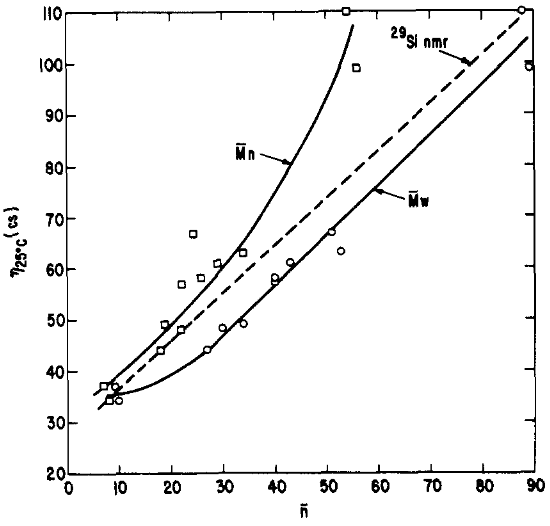


Figure 6. Comparison of GPC- and ^{29}Si NMR-derived correlations of block length with bulk viscosity for -OH terminated polydimethylsiloxanes.

Table II
GPC and ^{29}Si NMR Analyses of
$(CH_3)_3SiO-[(CH_3)_2SiO]_n-Si(CH_3)_3$ (M-D_n-M)

Sample	Mol wt	$\bar{M}_n$ (^{29}Si NMR)	$\bar{M}_n{}^a$	$\bar{M}_w{}^a$
M-D_5-M	533	540	513	518
M-D_6-M	607	630	610	618
M-D_9-M	829	873	848	864
SF-96(5)		859	750	810

[a] Corrected for Q factor ratio of 0.80.

When the GPC data shown in Figure 1 are replotted as $\overline{DP}$ vs. η, the apparent contradiction between the GPC and ^{29}Si NMR analyses is reconciled. Figure 6 compares this result (solid curves) with the ^{29}Si NMR values (dashed curve). The curves are nearly parallel. The bend at the low molecular weight end of the $\bar{M}_w$ curve may be due to column association phenomena. We do not wish to ignore the method in which the data were presented in Figure 1 since it is a perfectly valid approach. Nevertheless, this logarithmic treatment all too easily suggests a model of disiloxanol interactions which is inaccurate.

There are large discrepancies between the $\bar{M}_n$ values determined by GPC and by ^{29}Si NMR (Figure 6). In an attempt to understand the reasons for these discrepancies we analyzed by ^{29}Si NMR and GPC several authentic samples of monodispersed methyl-terminated polydimethyl siloxanes and a polydispersed 5 cs methyl-terminated fluid, SF-96(5). As can be seen from Table II, there is good agreement between the actual molecular weights and those values determined by ^{29}Si NMR values. To achieve similar agreement with the GPC values we had to employ an empirically derived Q-factor ratio of 0.80. The Q-factor ratio of 0.62 which we had used previously in the disiloxanol studies gave GPC molecular weights which differed considerably from the actual molecular weights. Except for the $\bar{M}_n$ values for SF-96(5), both analytical techniques are in good agreement. We conclude that the $\bar{M}_n$ discrepancies noted in the disiloxanol studies are attributable to differential spreading in the GPC by various disiloxanol species.

Experimental Section

NMR Measurements. The ^{29}Si Fourier transform spectra were obtained on a Varian XL-100-15 NMR spectrometer interfaced with a Transform Technology TT1020 high power amplifier operating at 19.86 MHz. All samples were run under proton noise decoupling conditions using deuterated solvents for the internal field frequency controlled lock system. Pulse widths of 45 μsec giving a flip angle of $\sim$60° were used to look at spectral windows of 1000 Hz with 4-sec acquisition times. Spectrometer control was obtained from the system computer (Varian 620i; 16K core) allowing acquisition of 8192 data points, resulting in 4096 output data points in the phase corrected absorption spectra. Samples were doped with about 0.1 M tris(acetylacetonato)chromium to shorten the T_1's by replacing ^{29}Si–^{1}H dipole–dipole (DD) and spin–rotation (SR) relaxation with electron nuclear DD relaxation resulting in T_1's of only a few seconds.[10]

Viscosity Measurements. Bulk viscosities were determined in Cannon-Manning semimicroviscometers in a bath thermostated at 25.0 ± 0.3°C.

Gel Permeation Chromatography Measurements. All samples were analyzed with a Waters Associates GPC 200; chromatograms were run using 0.5 wt % solutions in methylene chloride, injected over a 120-sec period. The GPC columns consisted of five columns in series packed with Styragel, having porosity ranges of 2.5 × 10^4, 2000–5000, 10^3, 350–700, and 60 Å. The columns were calibrated with standard polystyrene samples (Pressure Chemical Co.) of anionically polymerized polystyrenes and styrene monomer.

The Q factors and Q-factor ratio were calculated as follows. Polystyrene: $Q_{\mathrm{ps}} = 104$ g formula/2.51 Å = 41.5 g formula/Å. Polydimethylsiloxane: $Q_{\mathrm{PDMS}} = 74$ g formula/2.88 Å = 25.75 g formula/Å; $M_{\mathrm{PDMS}} = (25.75/41.5)(M_{\mathrm{ps}}) = 0.62M_{\mathrm{ps}}$.

Materials. All disiloxanols and monodispersed methyl-terminated fluids were provided by Dr. J. Razzano of the Silicone Products Business Department (SPBD), General Electric Co. The 5 cs fluid was General Electric SF-96(5) silicone fluid available from SPBD.

Acknowledgment. We wish to thank Drs. A. R. Shultz and P. C. Juliano for their helpful criticisms of this manuscript.

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Raman Spectrum of Crystalline Poly(*trans*-1,4-butadiene)

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ABSTRACT: Raman spectra of mats of poly(*trans*-1,4-butadiene) crystals grown at different temperatures have been obtained at 25°C. Spectra were also taken at temperatures in the 25–78°C region for one preparation and the changes in the Raman spectrum accompanying the transformation from form I to form II are described.

Poly(*trans*-1,4-butadiene) is known to have two crystalline forms; the form stable at room temperature and atmospheric pressure, form I, is reported to have a monoclinic lattice represented by the $P2_1/a$ space group and containing four chains.[1] Form II is stable (at atmospheric pressure) at temperatures between 71°C and the melting temperature; the distance between chains and the repeat distance along the chain is known from x-ray analysis.[2] The x-ray results and potential energy calculations[3] suggest that the polymer chains in form II of PTBD have considerable freedom of motion. In fact, the infrared spectrum found for form II is the same as that for PTBD in the melt or in solution.[4,5] A Raman spectrum for PTBD rubber containing 89% trans units and 9% cis units has been published.[6] A recent Raman study on form I crystals of PTBD has been carried out by Hsu, Moore, and Krimm;[7] in that investigation a normal vibration analysis of crystalline PTBD was also made.

In the present study the Raman spectra for mats of PTBD crystals grown from dilute solution have been obtained. The effects of crystal growth temperature and solvent and of various thermal and mechanical treatments on the spectrum at 25°C have been explored. Raman spectra at temperatures in the 25 to 78°C range have also been recorded and the changes accompanying the form I to form II crystal transition have been observed. These results are presented and discussed below.

Experimental Section

The characteristics of the polymer used in this investigation, PTBD-K, and the methods of crystal preparation have been reported on earlier.[8-13] The results of studies on the amorphous-crystalline content of crystals grown from dilute heptane and toluene solutions are given in Table I.

Raman spectra were obtained with a Spex Ramalog 3 employing an Argon laser. The wavelengths used were 4880 and 5145 Å. Slit widths of 1.7 to 4 cm^{-1} were employed. The crystal mats were