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SAND2002-3785

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Printed November 2002

Quantitative Analysis of Microstructure in Polysiloxanes Using High Resolution ^{29}Si NMR Spectroscopy: Investigation of Lot Variability in the LVM97 and HVM97 PDMS/PDPS Copolymers

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**Quantitative Analysis of Microstructure in Polysiloxanes Using
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Investigation of Lot Variability in the LVM97 and HVM97
PDMS/ PDPS Copolymers**

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Abstract

The quantitative analysis of microstructure and sequence distribution in polysiloxane copolymers using high-resolution solution ^{29}Si NMR is reported. Copolymers containing dimethylsiloxane (DMS) and diphenylsiloxane (DPS) monomer units prepared with either high vinyl content (HVM) or low vinyl content (LVM) were analyzed. The average run length (R_{exp}), the number average sequence length (l_A, l_B), along with the various linkage probabilities ($p_{AA}, p_{AB}, p_{BA},$ and p_{BB}) were determined for different production lots of the LVM97 and HVM97 samples to address the lot variability of microstructure in these materials.

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Acknowledgements

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000. The author is also indebted to Jim Schneider from Honeywell/FM&T for supplying different production lots of the HVM97 and LVM97 material.

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Nomenclature

DPS	diphenyl siloxane
DMS	dimethyl siloxane
NMR	nuclear magnetic resonance
R_{exp}	experimental <i>run</i> number
R_{rand}	random <i>run</i> number
l_A, l_B	average sequence length
p_{AB}	linkage probabilities
TMS	tetramethylsiloxane

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Introduction

The most commonly used silicone elastomer is poly(dimethyl siloxane) (PDMS). For a wide range of applications copolymers between PDMS and poly(diphenyl siloxane) (PDPS) have been shown to have superior thermal and physical properties. The addition of only a few percent PDPS suppresses the crystallization temperature to below $-100\text{ }^{\circ}\text{C}$, increases the refractive index for optical applications, and improves the thermal oxidative stability and resistance to radiation damage.¹⁻⁵

The thermal stabilities of PDMS/PDPS copolymers have also been extensively investigated.^{1,2} It has been shown that the addition of the diphenylsiloxane (DPS) component as a copolymer can increase the temperature for onset of degradation to approximately $400\text{ }^{\circ}\text{C}$. Thermal decomposition of the PDMS/PDPS copolymers is predominantly through the formation of cyclic oligomers containing both dimethylsiloxane (DMS) and DPS species, and the production of benzene as a result of thermally produced free radicals.²

A very interesting observation reported in the work of Chou and Yang, is that the microstructure (the sequential organization) of the PDMS/PDPS copolymer directly influences the thermal stability.¹ Chou and Yang demonstrated that random copolymers are more thermally stable than block copolymers, with the thermal stability increasing with higher DPS concentrations (to about 20% mol% DPS).¹ While there has been some research directly addressing the impact of the microstructure on thermal properties such

as the glass transition temperature (T_g) and crystallization temperature (T_m),¹ there has been very little research to address microstructural influences on aging properties; in particular the impact of microstructure in silicones. ***It may therefore become important to determine and document the actual microstructure of those materials for which the aging characteristics must be known and accurately predicted.***

In this SAND report we utilize high resolution ^{29}Si NMR to directly determine the microstructures of the LVM97 (low vinyl content material) and HVM97 (high vinyl content materials) silicones that are used as the precursor materials for the production of M9787 and M9750 cellular silicone foams. In addition, different production lots of the LVM97 and HVM97 materials were analyzed to address the question of lot-to-lot variability in the resulting microstructure of the PDMS/PDPS copolymers.

Experimental Details

A. Polysiloxane Materials

The polysiloxane samples were originally produced by Nusil (Carpenteria, CA), received and stored at Honeywell FM&T (Kansas City, KA), with a small sample being shipped to Sandia for analysis. The siloxane polymers consist of dimethyl (DMS), diphenyl (DPS), and methyl vinyl (MVS) siloxane monomer units. The approximate composition was 90.7 wt% DMS, 9.0 wt% DPS, and between 0.1 and 0.5% MVS. The variable vinyl content is designated in the LVM (low vinyl content) and HVM (high vinyl content) nomenclature used in the sample identification. The specific sample identification, part numbers and lot numbers are listed in **Table I**.

Table I. Sample Description

	Sample	Part #	Description	Lot #
#1	LVM97-A	4155867-00	LVM-97	1027981
#2	LVM97-B	4155867-00	LVM-97	1023011
#3	HVM97-A	4155868-00	HVM-97	0210981
#4	HVM97-B	4155868-00	HVM-97	0921991

B. NMR Analysis

The high resolution solution ^1H and ^{29}Si NMR spectra were obtained at a resonance frequency of 399.99 and 79.44 MHz, respectively on a Bruker DRX400 NMR spectrometer using a 5mm broad band probe. Typical ^1H NMR conditions were a $9.5\ \mu\text{s}$ $\pi/2$ pulse, 10s recycle delay and 16 scan averages. The ^{29}Si NMR spectra were obtained using with 1024 scans, a $7.5\ \mu\text{s}$ $\pi/2$ pulse, a 120 s recycle delay. A standard single pulse Bloch decay was used for all ^{29}Si experiments and utilized an inverse gated ^1H composite

pulse decoupling to suppress the negative NOE effect of ^{29}Si . No external relaxation agents were utilized. The ^{29}Si NMR spectra were referenced to external TMS ($\delta = 0.0$ ppm) at room temperature. For all experiments described approximately 100 mg of the polysiloxane materials was dissolved in 750 μl of CDCl_3 heated at 60 $^\circ\text{C}$. Spectral deconvolutions of the observed NMR resonances were performed using the commercial Bruker software XEDPLOT.

C. Theoretical Details of Microstructural Analysis

The determination of sequence distribution or microstructure in siloxane copolymers from ^{29}Si NMR has been previously described elsewhere.^{2,3} The mathematical formalism utilizing the relative areas of the different ^{29}Si NMR resonances has been very nicely described by Jancke, Englehardt and Heinrich,² including a correlation to the concept of the mean or average *run* length.⁴ A summary of those relationships is detailed below.

The probability distributions and signal intensities for the triad and pentad sequences are given in **Table II**. For the triad nomenclature the signal intensities are denoted by F_i , (or $[i]$) where i is the number of nearest neighbor monomer units of the second species in the copolymer. In the case of the PDMS/PDPS copolymer, if one is discussing the DMS ^{29}Si NMR signal then i corresponds to the number of DPS groups attached to the DMS monomer unit of interest. Conversely if one is discussing the analysis of the DPS signal, then i corresponds to the number of directly attached DMS monomer units. In the pentad nomenclature the different ^{29}Si signal intensities are

denoted by F_{ij} , or $[ij]$, where i is the number of directly attached monomer units of the other species and j is the number of next-nearest-neighbor of the other monomer species.

Table II. Probability Distributions and Signal Intensities for Triad and Pentad Sequences.

Triad		Triad Signal	Pentad		Pentad Signal
[0]	$p_{AA}^2 \cdot f_A$	F_0	[00]	$p_{AA}^4 \cdot f_A$	F_{00}
			[01]	$2p_{AA}^3 \cdot p_{AB} \cdot f_A$	F_{01}
			[02]	$p_{AA}^2 \cdot p_{AB}^2 \cdot f_A$	F_{02}
[1]	$2p_{AA} \cdot p_{AB} \cdot f_A$	F_1	[10]	$2p_{AA}^2 \cdot p_{AB} \cdot p_{BA} \cdot f_A$	F_{10}
			[11]	$2p_{AA}^2 \cdot p_{AB} \cdot p_{BB} \cdot f_A$ $2p_{AA} \cdot p_{AB}^2 \cdot p_{BA} \cdot f_A$	F_{11}
			[12]	$2p_{AA} \cdot p_{AB}^2 \cdot p_{BB} \cdot f_A$	F_{12}
[2]	$p_{AB}^2 \cdot f_A$	F_2	[20]	$p_{AB}^2 \cdot p_{BA}^2 \cdot f_A$	F_{20}
			[21]	$2p_{AB}^2 \cdot p_{BA} \cdot p_{BB} \cdot f_A$	F_{21}
			[22]	$p_{AB}^2 \cdot p_{BB}^2 \cdot f_A$	F_{22}

These F_i or F_{ij} concentrations can be related to the linkage probabilities as shown in **Table II**. The probability of an i - j linkage is defined by p_{ij} ($i, j = A, B$), where f_A is the mole fraction of the A monomer unit in the copolymer. For the PDMS/PDPS copolymer we can designate A = DMS and B = DPS. An analogous set of relationships for the triad and pentad signal intensities of the B monomer species can be derived by replacing f_A with f_B , and switching A for B in all the linkage probabilities. Following Harwood and Ritchey⁶ the molar concentration of the monomer units per 100 monomer units is defined by

$$\begin{aligned} A_M &= 100f_A \\ B_M &= 100f_B \end{aligned} \quad (1).$$

The ratio of triad signal intensities can be used to define the variable k_A through

$$k_A = 2 - 2\sqrt{\frac{F_0}{\sum F_k}} \quad (2).$$

The triad signal intensities F_k are the summation over related pentad signals

$$F_k = \sum_{l=0,1,2} F_{kl} \quad (3).$$

There are equivalent expressions for k_A involving different relative ratios as derived by Jancke *et al.*,⁷ but Eqn (2) was chosen because it involves the relative ratio of the dominant signal F_0 , and therefore was found to give the result with smallest error for the copolymer composition presently under investigation.

From these intensity ratios the average experimental *run* number for the copolymer can be determined using the formalism of Harwood,⁶ and is defined by

$$R_{exp} = k_A A_M \quad (4),$$

for the A monomer species. Similarly for the B monomer species the average experimental *run* number is also defined by

$$R_{exp} = k_B B_M \quad (5),$$

where k_B can be related back to the experimentally determined k_A in Eqn (2) by

$$k_B = k_A \frac{A_M}{B_M} \quad (6).$$

The average *run* number for a statistically random copolymer is given by

$$R_{rand} = \frac{A_M B_M}{50} \quad (7).$$

For $R_{exp} > R_{rand}$ the microstructure of the copolymer is a sequence of alternating monomer units, for $R_{exp} = R_{rand}$ the microstructure is random, and for $R_{exp} < R_{rand}$ the copolymer microstructure is a sequence containing blocks of the A and B monomer units.

By determining the average *run* number it is also possible to calculate the average block length of the A (l_A) and B (l_B) monomer species. The average block length is defined by

$$l_A = \frac{2A_M}{R_{exp}} \quad (8)$$

$$l_B = \frac{2B_M}{R_{exp}} \quad (9)$$

Results

An example of the high-resolution ^{29}Si NMR spectrum is shown in **Figure 1**, along with a molecular schematic of the silicon responsible for the different signals and the Triad and Pentad assignments. The two major resonances observed at $\delta \sim -21.6$ ppm and an $\delta \sim -47.4$ ppm correspond to dimethyl and diphenyl silicone species, respectively. Closer inspection of the dimethyl silicon region shows fine structure that can be assigned to the various configurations involving the presence of diphenyl species in the nearest and next-nearest-neighbor position using either the triad or pentad nomenclature.

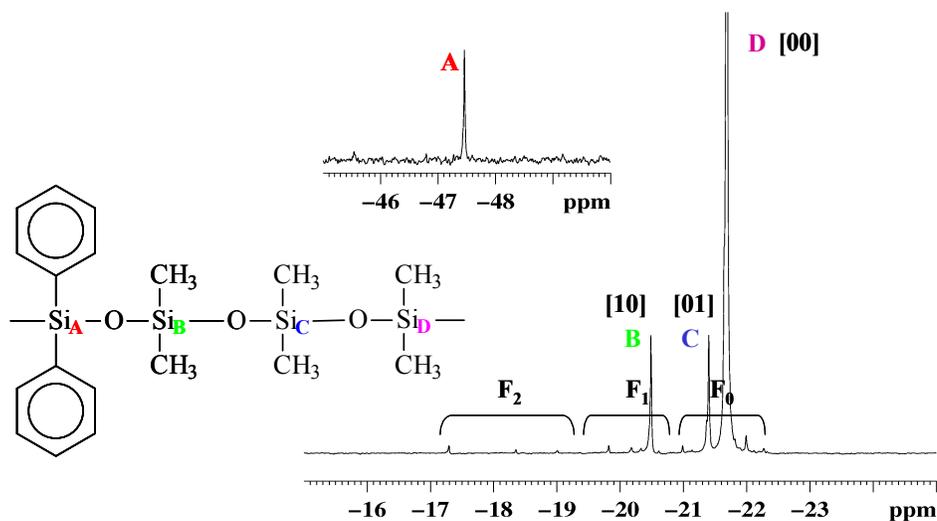


Figure 1: High-resolution ^{29}Si of HVM97 in CDCl_3 at 60°C

The integration of these different ^{29}Si NMR signals corresponds to the relative concentrations of the different Si species or environments. In this report we will use the DMS region of the ^{29}Si NMR spectra to determine the microstructure of the PDMS/PDPS copolymer. It would also be possible to determine the microstructure of the copolymer

from analysis of the DPS region, but the low wt% of the DPS component greatly reduces the intensity of this signal making quantitative integration very difficult. In addition, only the triad concentrations need to be determined (see **Figure 1**) instead of the individual Pentad concentrations since the calculation of the average *run* number and average block length only requires the triad concentrations. The relative concentrations of the DPS and DMS components were determined from integration of the high-resolution ^1H NMR spectra (not shown), which allowed the experimental determination of the mole and weight percent fractions, and are given in **Table III**.

Table III. Mole and Weight % Fraction of Monomers Obtained From ^1H NMR Analysis^a

Sample ID	A_M	B_M	A_W	B_W
LVM97-A	96.2 ± 0.1	3.8 ± 0.1	0.904 ± 0.001	0.096 ± 0.001
LVM97-B	96.0 ± 0.1	4.0 ± 0.1	0.900 ± 0.001	0.100 ± 0.001
HVM97-A	96.0 ± 0.1	4.0 ± 0.1	0.901 ± 0.001	0.099 ± 0.001
HVM97-B	96.2 ± 0.1	3.8 ± 0.1	0.905 ± 0.001	0.095 ± 0.001

^a A_M = mole % of the dimethylsiloxane monomer unit, B_M = mole % of the diphenylsiloxane monomer unit, A_W = weight fraction of the dimethylsiloxane monomer component, and B_W = weight fraction of the diphenylsiloxane monomer component.

Figure 2 shows the ^{29}Si NMR spectra for the different HVM and LVM lots (see **Table I**). The experimentally determined Triad concentrations for the different lots are listed in **Table IV**. The microstructural parameters described from Eqns 1 – 9 were evaluated for the different production lots and are summarized in **Table IV**.

Table IV. Microstructural Parameters for HVM97 and LVM97 Samples Using High Resolution ^{29}Si NMR^a

Microstructural Parameter	LVM97-A	LVM97-B	HVM97-A	HVM97-B
A_M^b	96.2 ± 0.1	96.0 ± 0.1	96.0 ± 0.1	96.2 ± 0.1
B_M^b	3.8 ± 0.1	4.0 ± 0.1	4.0 ± 0.1	3.8 ± 0.1
F_2	0.10 ± 0.5	0.10 ± 0.5	0.1 ± 0.5	0.1 ± 0.5
F_1	7.25 ± 0.5	7.78 ± 0.5	7.42 ± 0.5	7.88 ± 0.5
F_0	92.65 ± 0.5	92.12 ± 0.5	92.48 ± 0.5	92.02 ± 0.5
R_{rand}	7.4	7.7	7.6	7.2
R_{exp}	7.1	7.6	7.3	7.7
l_A	27.1	25.0	26.4	24.9
l_B	1.1	1.0	1.1	1.0
p_{AA}	0.963	0.960	0.962	0.960
p_{AB}	0.037	0.040	0.038	0.040
p_{BB}	0.073	0.048	0.083	<0.001
p_{BA}	0.927	0.953	0.917	1.029

^a Definition of microstructural parameters given in theory section, Eqn (1)-(9). ^b Mole % fractions determined from ^1H NMR, see Table III.

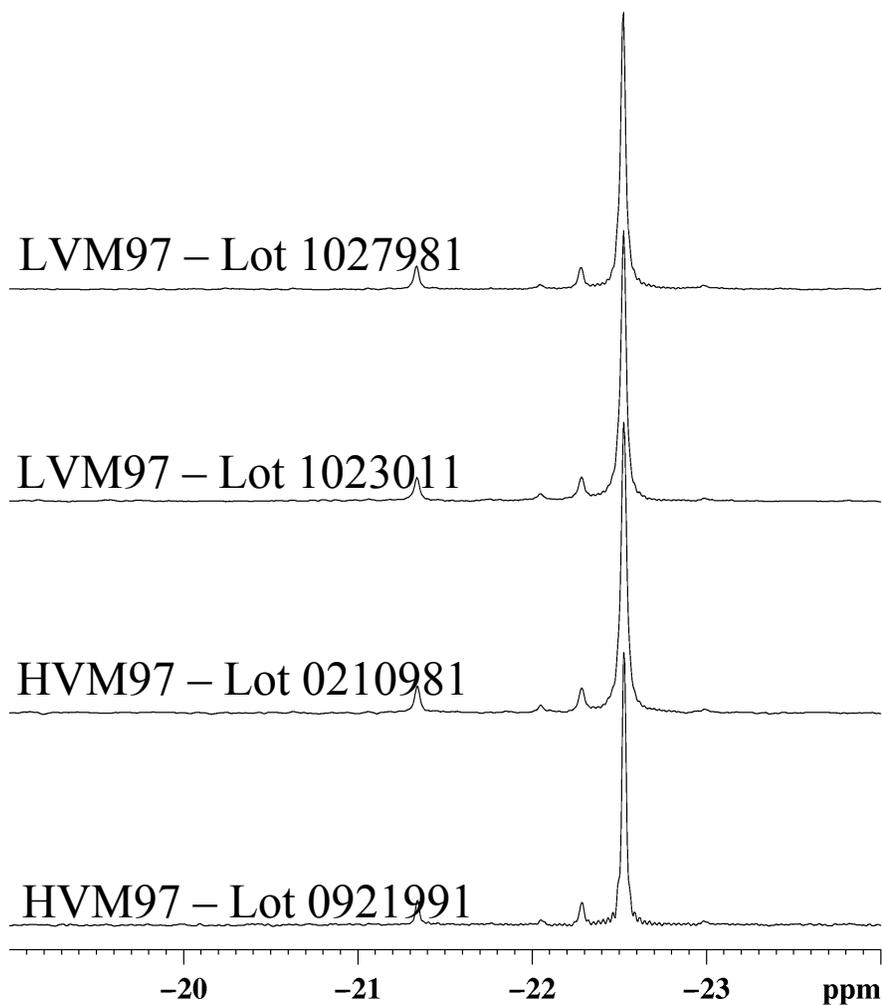


Figure 2: High-resolution ^{29}Si NMR for different production lots of LVM97 and HVM97.

Discussion

For all the samples investigated the experimentally determined average *run* number were found to be approximately equal to the predicted random *run* number based on the measured mole fractions (**Table IV**). These results are graphically shown in **Figure 3**. This result demonstrates that the HVM97 and LVM97 PDMSD/PDPS copolymers are statistically random in nature, with the deviation being within experimental error. There does not appear to be any large deviation in the observed *run* number with production lot.

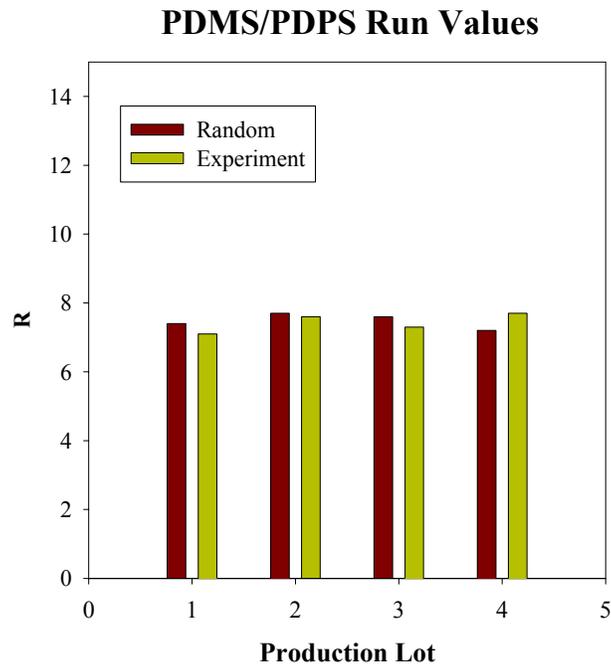


Figure 3: Experimentally determined R_{exp} for different production lots, with 1,2,3,4 corresponding to the order ted in **Table I**.

The average DMS average block length was found to range from 24.9 to 27.1. These DMS average block lengths are plotted in **Figure 4** along with the block lengths predicted for a statistically random copolymer, demonstrating that these results are also consistent with the description of the LVM97 and HVM97 materials as random copolymer. The average block length for the DPS species is $l_B \sim 1$ (**Table IV**), demonstration that the DPS species are essentially isolated from other DPS species, and are surrounded entirely by DPS species. This clearly shows that the original octaphenyltetracyclosiloxane use in the synthesis is completely fragmented during the polymerization process, without any significant concentration of single ring opening reactions occurring.

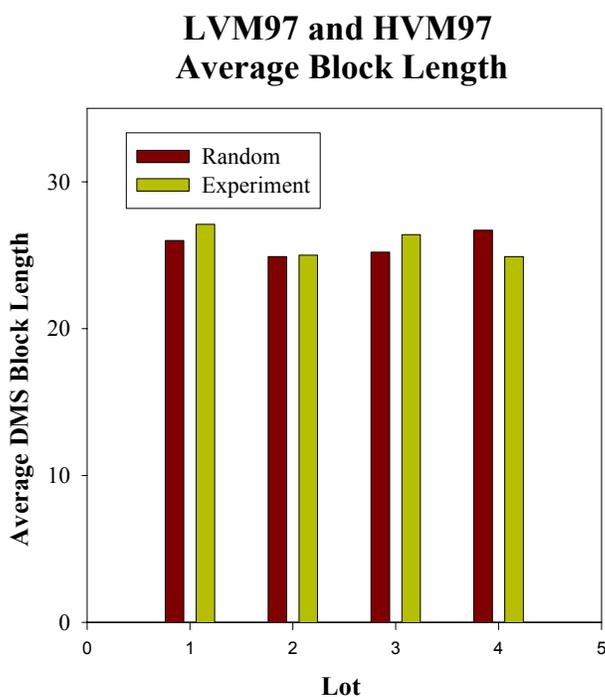


Figure 4: Average block length for the DMS species in the PDPS/PDMS copolymer as a function of production lot.

Conclusions

It has been demonstrate that high-resolution ^{29}Si NMR can be used to determine and monitor the microstructure in PDMS/PDPS copolymer materials. These ^{29}Si NMR experiments show that for the HVM97 and LVM97 materials studied that the copolymer is entirely random in nature. These NMR studies also show that there was no significant variation in the microstructure with different production lots, or with the inclusion of different vinyl content. This observation supports the argument that variations in microstructure are not responsible for differential changes in the aging characteristics of these siloxane materials.

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