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Structural Analysis of Poly(tetramethyl-*p*-silphenylenesiloxane)–Poly(dimethylsiloxane) Copolymers by ^{29}Si NMR

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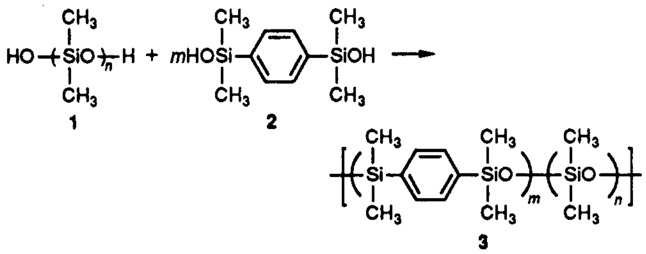
ABSTRACT: A method for measuring composition and sequence lengths in poly(dimethylsiloxane)/poly(tetramethyl-*p*-silphenylenesiloxane) copolymers by ^{29}Si NMR is presented. The technique has been used to study the relationship between the block length in the copolymer and the degree of oligomerization of the starting disiloxanol, and to study the redistribution reaction of the polymer. It has been shown from ^{29}Si NMR studies of the polymerization reaction that efficient water removal is necessary to minimize redistribution of siloxane bonds in the polymer.

Introduction

The block copolymers of poly(dimethylsiloxane) (DMS) and poly(tetramethyl-*p*-silphenylenesiloxane) (TMPS) exhibit a wide range of properties depending upon the composition and average sequence lengths of the soft dimethylsiloxane segments and the hard crystalline silphenylene blocks. Since the pioneering studies of the synthesis and properties of these polymers by Merker and coworkers,[1,2] a wide variety of silarylene–siloxane copolymers[3] have been prepared. The synthesis of the TMPS–DMS copolymers (3) typically involves the condensation polymerization of an α,ω-dihydroxypoly(dimethylsiloxane) (1) with 1,4-bis(hydroxydimethylsilyl)benzene (2) using a catalyst designed to avoid equilibration and siloxane bond breaking. Block lengths can be varied by changing the stoichiometry of the polymerization and by using starting disiloxanol fluids, 1, with different degrees of polymerization. The characterization of these materials has traditionally been accomplished by use of ^{1}H and ^{13}C NMR and by measurement of physical properties. In addition, the final block length of the dimethylsiloxane portion of the polymer has often been inferred from the degree of polymerization of the starting disiloxanol. Since physical properties are dependent upon block lengths as well as composition of the polymer, it is important to be able to measure this structural parameter in order to develop an understanding of the structure/property relationships in these materials.



In this paper we report the use of ^{29}Si NMR as a technique for measuring compositions and block lengths in the silphenylene–siloxane copolymers[4] and as a method for monitoring the polymerization reaction. The technique has been used to (1) determine the relationship between the block length in the copolymer and the degree of oligomerization of the starting disiloxanol, (2) determine if condensation catalysts are also redistribution catalysts during the course of the polymerization, and (3) establish the true structure of exactly alternating copolymers.

Experimental Section

General Information. The α,ω-dihydroxypoly(dimethylsiloxanes), $Me_2Si(NMe_2)_2$, and 1,3-dichlorotetramethyldisiloxane were purchased and used as received. The exactly alternating TMPS–DMS copolymer was prepared by reaction of equimolar amounts of $Me_2Si(NMe_2)_2$ and 2 according to the method of Burks et al.[8] The condensation catalyst used to prepare TMPS–DMS copolymers was synthesized according to the procedure in ref 2.

Preparation of 1,3-Dihydroxytetramethyldisiloxane (4). 1,3-Dichlorotetramethyldisiloxane (50 g, 0.246 mol) was added dropwise to a stirred solution of water (1 L) and diethyl ether (500 mL) cooled to 0 °C. Care was taken to protect the chlorosiloxane from hydrolysis prior to the addition. NaOH (1 M) was added concurrently with the chlorosiloxane to the reaction

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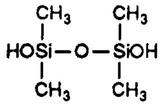


$$\mathrm{HO\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}OH}$$

4

to maintain a neutral pH, using methyl orange as the indicator. The two phases were separated, and the water layer was washed several times with ether. The ether solutions were combined, and the volatiles were removed in vacuo to yield a colorless oil. This oil was found to contain the product in addition to impurities composed of silicone cyclics.

Separation was achieved by dissolving this oil in hexane (100 mL) and extracting the product into water. NaCl was added to the water extracts, and the solution was cooled below 0 °C. After several hours at this temperature, white needlelike crystals precipitated and were collected by filtration. The product was dried and recrystallized from hexane/ether to produce 12 g (29% yield) of **4** [mp 67–68 °C (lit.[6] mp 68.5 °C)]. The high purity of the product was confirmed by ^{29}Si NMR (see Figure 3). This synthesis gave consistently higher yields than an earlier literature preparation.[6]

Preparation of 2. The silphenylene monomer was prepared by hydrolysis of 1,4-bis(*n*-propoxydimethylsilyl)benzene,[7] which was, in turn, prepared by reaction of *p*-dichlorobenzene, Mg, and di-*n*-propoxydimethylsilane.[9] The experimental details of this improved synthesis are described below.

Preparation of 1,4-Bis(*n*-propoxydimethylsilyl)benzene. A 2-L three-necked flask containing fresh Mg turnings (69.2 g, 2.88 mol) was heated above 100 °C for several minutes under a purge of nitrogen. $Me_2Si(On\text{-}Pr)_2$ (500 g, 2.82 mol), *p*-dichlorobenzene (207.6 g, 1.41 mol), dry THF (50.8 g, 0.705 mol), and a crystal of I_2 were added to the flask. The reaction mixture was heated slowly to 130 °C with mechanical stirring. Evidence for reaction initiation was provided by the formation of a yellow color, a precipitate, and an exotherm. External heat was removed, and the heat of reaction maintained reflux at 130 °C for 3–4 h. The mixture was maintained at this temperature for an additional 12 h. After cooling, the product was filtered away from the Mg salts, and the salts were washed several times with pentane. The combined filtrates were vacuum distilled, and the product was collected at 146–149 °C (<1 mm). The yield of 1,4-bis(*n*-propoxydimethylsilyl)benzene was 275 g (63%). This reaction has been performed on a larger scale (6 mol of *p*-dichlorobenzene) for which yields of 1,4-bis(*n*-propoxydimethylsilyl)benzene as high as 79% have been obtained.[7]

Preparation of 1,4-Bis(hydroxydimethylsilyl)benzene (2). The di-*n*-propoxysilphenylene derivative was hydrolyzed by dissolving the product of the above reaction (275 g, 0.887 mol) in 300 mL of acetone. Water (200 mL) was added followed by a small quantity of butyl ammonium formate ($n\text{-}BuNH_3{}^+O_2CH^-$) (0.20 g). No hydrolysis was observed in the absence of a hydrolysis catalyst. The reaction was stirred at 25 °C for 12 h. The acetone was removed in vacuo, and upon addition of more water (500 mL), a large amount of colorless crystals formed. This material was collected by filtration, dried, and recrystallized from hot toluene to give 181 g (91%) of **2**. The identity of the product was confirmed by comparison of melting point (mp 132–134 °C) and ^{29}Si NMR chemical shift (see Figure 3) with an authentic sample (Petrarch).

Preparation of TMPS–DMS Copolymers. 1,3-Dihydroxytetramethyldisiloxane (**4**) (5.0 g, 30 mmol) and **2** (6.81 g, 30 mmol) were dissolved together in 6.09 g of toluene. The condensation catalyst, ($[Me_2NC(=NH)NMe_2H^+Me(CH_2)_3CH(Et)CO_2{}^-]$) (tetramethylguanadinium 2-ethylhexanoate), was added (0.5% by weight, 0.059 g), and the reaction was heated to reflux for 12 h. The water condensate was collected in a Dean–Stark trap that was initially filled with toluene. The viscous solution containing the copolymer was precipitated into a large amount of MeOH with rapid stirring using a blender. The polymer was collected by filtration and further dried in a vacuum oven.

The other TMPS–DMS copolymers were prepared in identical reactions except for substitution of α,ω-dihydroxypoly(dimethylsiloxanes) of varying chain lengths. All of these copolymers were characterized by the ^{29}Si NMR technique described in the text. The isolated yields of the copolymers obtained from these reactions were greater than 95% with the exception of polymers prepared from α,ω-dihydroxypoly(dimethylsiloxanes) with short average chain lengths ($n = 2$ and 6). The yields for these polymers were 89 and 93%, respectively, with losses probably due to the formation of cyclic poly(dimethylsiloxane) oligomers.

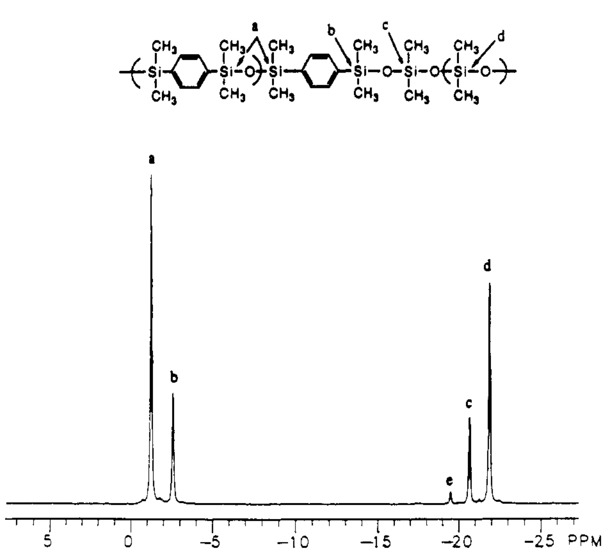


Figure 1. Silicon-29 NMR spectrum of a silphenylene–siloxane block copolymer (67 mol % DMS) with average silphenylene block length, $\bar{n}_{TMPS} = 4$, and average dimethylsiloxane block length, $\bar{n}_{DMS} = 7$. Peaks correspond to DMS and TMPS block silicon atoms labeled in the structure and in the text.

NMR Measurements. Silicon-29 NMR spectra were obtained on a Varian XL-300 NMR spectrometer operating at 59.6 MHz for ^{29}Si. Samples were run as 20 w/v % solutions in deuteriochloroform for 500–7000 scans as necessary to obtain adequate signal/noise for quantitation. Typical parameters included a 16-kHz spectral width, pulse width corresponding to a 45° flip angle, 32K data points, and a 1-s recycle delay for qualitative measurements and 5-s delay for quantitative spectra. A small amount (ca. 75 mg) of chromium(III) acetylacetonate was added as a relaxation reagent to shorten the ^{29}Si spin–lattice relaxation times (T_1), and gated decoupling was used to eliminate the negative nuclear Overhauser effect (NOE). The 5-s recycle delay, relaxation reagent, and gated decoupling were all necessary to ensure that quantitative data were obtained. All ^{29}Si chemical shifts are reported relative to internal tetramethylsilane (TMS) with positive values to lower field (deshielded) and negative values to higher field (shielded).

Results and Discussion

The silicon-29 NMR spectrum of a TMPS–DMS (67 mol % DMS) block copolymer is shown in Figure 1. The peaks at −1.27 and −2.62 ppm arise from the TMPS portion of the copolymer, and the peaks at −20.70 and −21.93 ppm are due to the DMS component. The assignments were made based on known ^{29}Si chemical shifts.[5] Examination of polymers of varying composition and estimated block length confirmed the assignments. The average block lengths of the TMPS ($\bar{n}_{TMPS}$) and DMS ($\bar{n}_{DMS}$) sequences can be calculated from the integrated intensities of the peaks in the spectrum as follows:

$$\bar{n}_{DMS} = 2(d/c) + 2 \quad (1)$$

$$\bar{n}_{TMPS} = (a/b) + 1 \quad (2)$$

As expected, the precision of the measurement is much better for the short block copolymers. In measuring a silphenylene block of an average value of 17.0 units, for example, a standard deviation of 0.36 was obtained for six measurements. For the siloxane block in the same polymer, the average block length was calculated to be

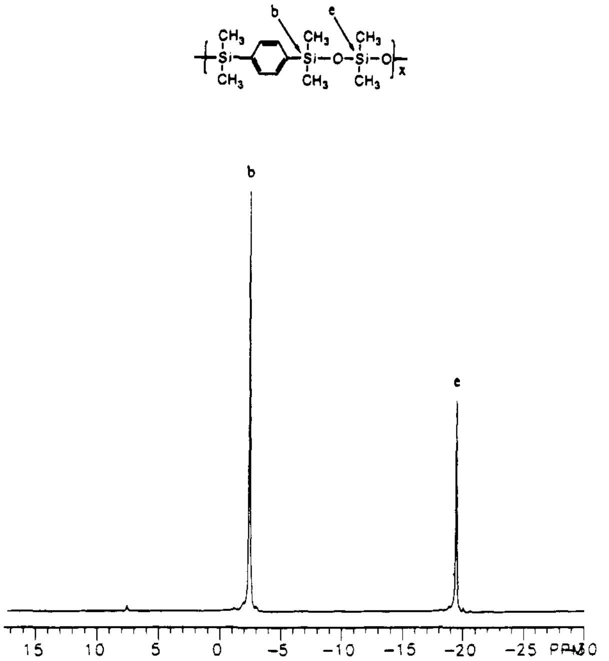


Figure 2. Silicon-29 NMR spectrum of exactly alternating TMPS-DMS copolymer prepared according to the method of Burks et al.[8] Labels correspond to silicon atoms shown in Figure 1 and in the text.

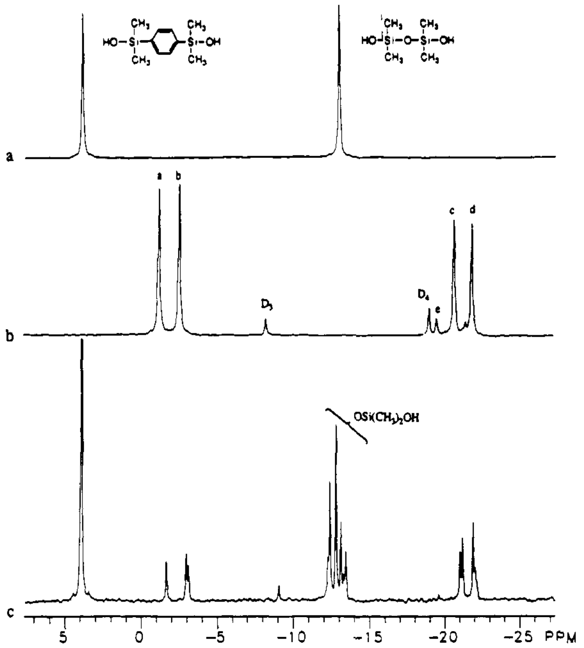
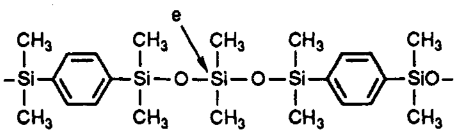


Figure 3. Silicon-29 NMR spectra monitoring the polymerization reaction between **2** and **4** (labels as in Figure 1): (a) starting materials; (b) after 1 h with water continuously removed; (c) after 1 h with no water removal.

47.0 units. The standard deviation for these six measurements, however, was 1.81.

In addition to the normal block terminal units for the TMPS and DMS sequences (b and c, respectively), the ^{29}Si spectrum contains a peak at −19.57 ppm (e) for most of the polymers examined. This has been attributed to the presence of single DMS units isolated between two TMPS units:



This was confirmed by examining the exactly alternating polymer prepared by reaction of $Me_2Si(NMe_2)_2$ and **2** according to the method of Burks et al.[8] The reaction proceeded cleanly to produce unique TMPS and DMS units, which gave rise to the two ^{29}Si resonances shown in the spectrum in Figure 2. The peak for the dimethylsiloxy group appears at −19.6 ppm, a shift which is identical with that assigned for this type of structural unit in the spectra of the block copolymers. It should be noted that the calculation of block length for the DMS blocks in eq 1 does not take these "blocks" of one unit into account. In most of the polymers we examined, only a small number of isolated DMS units were present and did not drastically affect the calculated average block length. However, these units may serve to increase the effective length of the crystalline silphenylene blocks rather than acting as "soft" blocks of one unit, thereby affecting the properties of the polymer in an unexpected fashion.

In order to test the effect of water on the polymerization reaction, equimolar amounts of the tetramethyldisiloxane (**4**) and tetramethyl-*p*-silphenylene (**2**) diols were reacted in refluxing toluene in the presence of a mild condensation catalyst both with and without azeotropic removal of water (Figure 3a–c). Figure 3a shows the ^{29}Si spectrum of the starting siloxanols. The block lengths in the polymer resulting from the reaction with rapid water removal were measured from the ^{29}Si NMR spectrum shown in Figure 3b. The presence of cyclic dimethylsiloxane trimer (D_3) and tetramer (D_4) shows that some cyclic species are formed during the condensation polymerization. The block lengths were found to be twice that of the starting materials, i.e., approximately 4 for the dimethylsiloxane blocks (the starting material has a chain length of 2) and 2 for the tetramethyl-*p*-silphenylenesiloxane blocks. A small amount of single DMS units between TMPS units (at 19.6 ppm) was also detected, indicating that some redistribution had taken place. The effect of water on the polymerization of **2** and **4** is shown in Figure 3c. Both parts b and c of Figure 3 show the ^{29}Si NMR spectrum of the reaction products of the polymerization after 1 h. In the product shown in Figure 3c, however, water was not removed from the reaction. Whereas the reaction in which water was removed was virtually complete after 1 h as shown in Figure 3b (no residual starting materials or silanols were detected), the reaction in which water was not removed (shown in Figure 3c) contains starting material, cyclics, and low molecular weight silanols. Clearly, the removal of water is necessary to drive the reaction to completion and prevent the formation of side products.

Water also plays a major role in the redistribution reaction as shown in Figure 4. When a polymer of average block lengths $\bar{n}_{DMS} = 32$ and $\bar{n}_{TMPS} = 17$ was placed in toluene at 110 °C in the presence of catalyst, no changes were observed after 5 days (Figure 4a). In the presence of a small amount of water, however, the block lengths dropped significantly in the same period of time to approximately one-fourth of the original value (Figure 4b). Both of these polymers were precipitated from methanol prior to NMR analysis. The constant TMPS-DMS ratio before and after reaction indicates that the formation of cyclic oligomers (D_3, D_4, D_5) was not extensive. Cyclic formation was apparently not favored at these high polymer concentrations.

Since water is a product of the polymerization, it is impossible to remove it completely during the synthesis of these polymers. As a result, the final block lengths in the polymer will be dependent upon several factors such

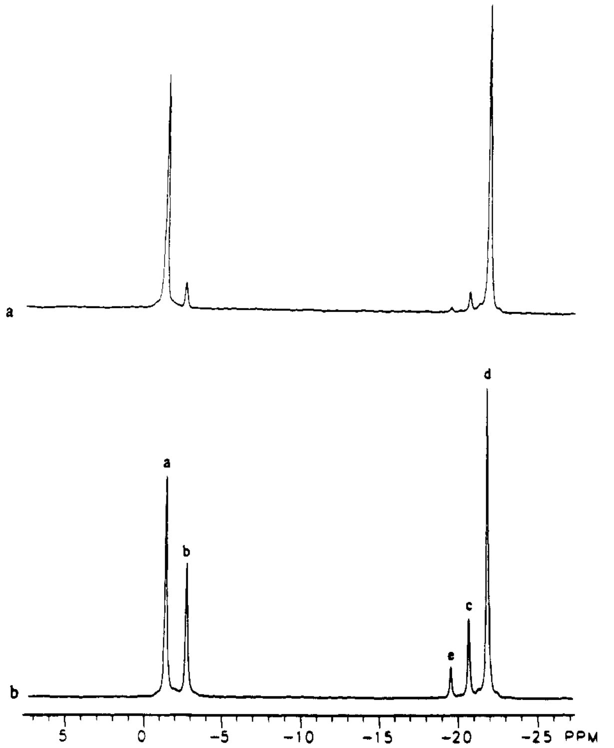


Figure 4. Silicon-29 NMR spectra showing the effect of water on the redistribution reaction (labels as in Figure 1): (a) polymer in toluene at 110 °C in the presence of catalyst but no water after 5 days; (b) same conditions but with a few drops of water added.

as reaction stoichiometry, degree of oligomerization and composition of the starting α,ω-dihydroxypoly(dimethylsiloxane), and the amount of water present during the reaction. In order to determine if a minimum sequence length could be expected based on the chain length of the starting hydroxy-terminated dimethylsiloxane oligomer (i.e., no redistribution of the siloxane chain occurred during the polymerization), the chain lengths of a series of oligomers were measured by using ^{29}Si NMR[5] and then compared with the DMS block lengths in the copolymers after polymerization. The results are collected in Table I. All of the polymers were prepared to be 67 mol % DMS. It is apparent from the decrease in the DMS chain length in the higher oligomers that the use of a "nonequilibrating" catalyst does not prevent redistribution of the siloxane chains, although under certain conditions redistribution is slow relative to condensation. Thus, a minimum DMS block length in the polymer cannot be inferred from the chain length of the oligomer from which it is synthesized, at least under these polymerization conditions.

Table I
Average Dimethylsiloxane (Me_2SiO-) Sequence Lengths in Disiloxanol and Resulting Copolymer As Measured by ^{29}Si NMR

$HO(SiMe_2)_nOH$: $\bar{n}$	TMPS-DMS copolymer: $\bar{n}_{DMS}$	$HO(SiMe_2)_nOH$: $\bar{n}$	TMPS-DMS copolymer: $\bar{n}_{DMS}$
2	4	55	32
6	7	260[a]	95[a]

[a] Values are approximate since sequence lengths >70 are difficult to measure with reasonable precision. Although the error may be as high as ±10–15 units, there is unquestionably a decrease in sequence length that occurs during the preparation of the polymer.

Conclusions

Silicon-29 NMR provides an excellent method for determining composition and block lengths in TMPS–DMS copolymers and for monitoring the course of the polymerization reaction. It is clear from ^{29}Si studies of the polymerization that efficient water removal from the reaction is necessary to minimize redistribution since condensation catalysts are also redistribution catalysts when water is present. Furthermore, the block length of the DMS portion of the copolymer is dependent upon a number of factors and cannot be assumed from the chain length of the starting disiloxanol fluid.

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Registry No. (2)(4) (alternating copolymer), 132102-72-8; **2**, 2754-32-7; **4**, 1118-15-6; $Me_2Si(O\text{-}n\text{-}Pr)_2$, 5621-09-0; 1,3-dichlorotetramethyldisiloxane, 2401-73-2; *p*-dichlorobenzene, 106-46-7; 1,4-bis(*n*-propoxydimethylsilyl)benzene, 59892-98-7.