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Poly(dimethylsiloxane-*co*-diphenylsiloxanes): Synthesis, Characterization, and Sequence Analysis

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ABSTRACT: Poly(dimethylsiloxane-*co*-diphenylsiloxane) copolymers have been prepared by ring-opening and step-growth condensation polymerizations. Composition of the copolymers has been determined by ^1H and ^{29}Si NMR spectroscopy. Sequence distribution up to the pentad level is observable in the ^{29}Si NMR spectrum. Copolymers have been characterized by GPC and DSC measurements. The glass transition temperatures increase with an increase in the proportion of diphenylsiloxane content.

Introduction

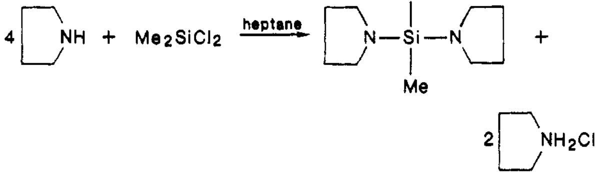
Silicone elastomers have long been known for their exceptional ability to exhibit and retain superior mechanical properties over a broad temperature range.[1] The main interest in these materials stems from the fact that they possess unique properties such as good low-temperature flexibility, excellent electrical properties, chemical inertness, water repellency, and biocompatibility not common in hydrocarbon polymers.[2,3] Various structural modifications have been investigated in order to modify some of the properties. For example reinforcement by silica fillers help in modifying the weak cross-linked network of conventional silicone rubber.[4] Segmented copolymers comprising hard and soft segments are an alternative approach to obtain polymers with specific end uses.[5-7] Synthesis of low and high molecular weight poly(dimethylsiloxane-*co*-diphenylsiloxanes) have also been reported.[8-10] It has been shown that introduction of diphenylsiloxane segment usually disrupts the low-temperature crystallization of polydimethylsiloxane and also increases the thermal and radiation stability.[1] There has been no systematic study of the structure-property relationship of these novel copolymers. The objective of this investigation is to synthesize and characterize high molecular weight poly(dimethylsiloxane-*co*-diphenylsiloxanes) and determine their sequence by ^{29}Si NMR spectroscopy. An attempt has also been made to correlate sequence distribution with the physical properties of the copolymers.

Experimental Section

Spectra. Proton and ^{29}Si NMR spectra were obtained on Varian XL-100 and XL-400 NMR spectrometers, respectively, at 100 MHz (^1H) and 79.46 MHz (^{29}Si). Chemical shifts are given relative to tetramethylsilane internal reference. Integrals on the proton spectra were obtained directly on concentrated solutions in chloroform-*d*. Ten milligrams (0.01 M) $Cr(acac)_3$ relaxation reagent was added to each 3 cm^3 solution of the samples before the ^{29}Si spectra was obtained in order to eliminate the nuclear Overhauser enhancement and reduce the relaxation times (T_1). Measurement of T_1 and nOe on a representative sample indicated all silicons in the polymer multiplets had comparable T_1 values of 5.0 s and that the nOe was 0.9. Quantitative ^{29}Si spectra were obtained by using 35° pulses and a 1.9-s recycle time to maximize the signal/noise. This partial saturation of the peaks will not effect integrals used to calculate the sequence distribution since all the polymeric absorptions had similar relaxation times. Also, the ratios of $SiPh_2O$:$SiMe_2O$ observed in the ^1H spectra match those observed in the ^{29}Si spectra.

Materials. Octamethylcyclotetrasiloxane (methyl tetramer, D_4), octaphenylcyclotetrasiloxane (phenyl tetramer, D_4^{Ph}), and diphenylsilanediol (DSD) were obtained from Petrarch Systems or Silar Laboratories. Bis(dimethylamino)dimethylsilane and 1,7-bis(dimethylamino)hexamethyltrisiloxane (Silar Lab.) were freshly distilled before use.

Synthesis. Bis(pyrrolidinyl)dimethylsilane. A dry 1-L three-necked, round-bottom flask was fitted with a reflux condenser, dropping funnel, mechanical stirrer, and an argon inlet. The apparatus was degassed by alternately evacuating and filling with argon. With argon flow through the system, freshly distilled dimethyldichlorosilane (90 g, 0.7 mol) and dry heptane (150 mL) were placed in the reaction vessel (eq 1). Dry pyrrolidine (199 g, 2.8 mol) was added dropwise over a period of 3 h with stirring and cooling in an ice bath. After completion of the addition, the reaction mixture was stirred overnight at ambient temperature. The amine hydrochloride precipitate was removed by filtration with positive argon pressure. The solvent was removed under vacuum. The residue was distilled at 85–87 °C (0.1 mm) in 95% yield: IR (neat) C–H, 3000, 2960, 2875 cm^{-1} (s, s, s); Si–Me, 1265 cm^{-1} (s), Si–N, 995 cm^{-1} (m).



(1)

Bis[phenyl(1-pyrrolidinylcarbonyl)amino]dimethylsilane[11,12] **(Referred to as Diureidosilane).** A 1-L, three-neck round-bottom flask was equipped with mechanical stirrer, an argon inlet, a reflux condenser, and a dropping funnel. The apparatus was alternately evacuated and filled with argon six to eight times. Freshly distilled dipyrrolidinyldimethylsilane (100 g, 0.5 mol) and 350 mL of dry ether were added, and the mixture was stirred in a 0–5 °C ice bath for approximately 10 min (eq 2). Dry phenyl isocyanate (119 g, 110 mol) was added to the chilled solution over a 1-h period. A white solid slowly separated during addition. Stirring was continued for an additional 3 h to ensure the completion of the reaction. The compound was then filtered under positive argon pressure and washed with dry pentane. The product was isolated in 90% yield: mp 125 °C lit.[11] mp 124–125 °C. Purity of the product was confirmed by elemental analysis. IR (KBr): C–H, 3000, 2960, 2875 cm^{-1} (s, s, s), Si–Me, 1260 cm^{-1} (s), N–H, 3475 cm^{-1} (s).

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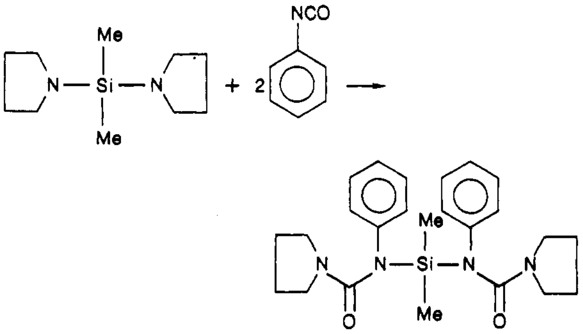
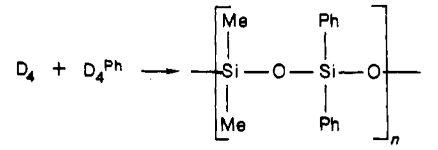


(2)

Polymer Synthesis. Ring-Opening Polymerization of Methyl Tetramer and Phenyl Tetramer (Polymers 1–5). Predetermined amounts of methyl tetramer and phenyl tetramer were charged to the reaction kettle (eq 3) fitted with a mechanical stirrer, thermometer, argon inlet, and dry ice condenser. The contents were heated to 165 °C in an oil bath. Polymerization was initiated by the addition of potassium hydroxide (10–25 ppm). The reaction mixture was heterogeneous during the first 3–4 h and became homogeneous as the reaction proceeded. The reaction was run from 15 to 24 h depending on the content of phenyl tetramer in the feed. At the end of the reaction, the catalyst was deactivated with acetic acid. The low molecular weight and the cyclic products were stripped off under vacuum. The copolymer was purified by repeated precipitation in methanol from toluene solution. The purified polymer was dried under vacuum at 80 °C to constant weight. The yields in all cases were greater than 80%.



$$D_4 + D_4^{Ph} \longrightarrow \left[\begin{matrix} Me & & Ph & \\ | & & | & \\ Si & -O- & Si & -O \\ | & & | & \\ Me & & Ph & \end{matrix} \right]_n$$

(3)

Preparation of Poly(dimethylsiloxane-*co*-diphenylsiloxane) from Diphenylsilanediol and Bis(dimethylamino)dimethylsilane (Polymer 6).[13] Diphenylsilanediol (15 g, 0.0694 mol) was placed in a weighed three-necked 250-mL round-bottom flask and dried overnight in a vacuum oven at 50 °C. The flask was reweighed, fitted with a thermometer, a mechanical stirrer, and a two-outlet adaptor supporting a reflux condenser and a septum-sealed opening. The system was then alternately evacuated and filled with argon several times. To the flask was added 50 mL of dry toluene while positive argon pressure was maintained. The reaction mixture was heated to a gentle reflux. Under argon atmosphere, 10.13 g (0.0694 mol) of bis(dimethylamino)dimethylsilane was withdrawn into a dried, preweighed syringe. The silane was injected through the septum into the reaction flask. Approximately 2.5 g of silane was added to the flask. This addition was repeated four times over 24-h period. The remaining silane (0.1–0.2 g) in the syringe was diluted with 2 mL of dry toluene and was added twice in a 6-h period. The reaction was further refluxed for 4 more hours. The viscous polymer solution was precipitated in 500 mL of methanol. The polymer was further purified and dried at 80 °C under vacuum to constant weight. Low tack opaque polymer was obtained in 65% yield. IR (neat): C–H, 3000, 2960, 2875 cm^{-1} (s, s, s), Si–Me, 1260 cm^{-1} (m), Si–O–Si, 1060–1110 cm^{-1} (s), Ph–Si<, 1180, 985, 740 cm^{-1} (m, m, m).

Preparation of Poly(dimethylsiloxane-*co*-diphenylsiloxane) from Diphenylsilanediol and 1,7-Bis(dimethylamino)hexamethyltrisiloxane (Polymer 7). The preparation of polymer 7 was carried out following the method described for polymer 6. Polymer 7 was precipitated twice with methanol and recovered in 69% yield. IR (neat): C–H 3000, 2960, 2875 cm^{-1} (s, s, s), Si–Me, 1260 cm^{-1} (s), Si–O–Si, 1060–1110 cm^{-1} (s), Ph–Si, 1180, 898, 742 cm^{-1} (m, m, m).

Preparation of Poly(dimethylsiloxane-*co*-diphenylsiloxane) from Diphenylsilanediol and Diureidosilane (Polymer 8). Diphenylsilanediol (15 g, 0.0694 mol) was dried in a 250-mL flask as described before. After the flask was fitted with thermometer, additional funnel, mechanical stirrer, and argon inlet, dried chlorobenzene (15 mL) was added to the diol and the flask was cooled to 0 °C. Bis(ureido)silane (30.53 g in 40 mL of chlorobenzene) was added portionwise over a 6-h period through the addition funnel. The reaction was allowed to continue at ambient temperature overnight. The solid reaction byproduct was removed by filtration. The solution was concentrated. The siloxane polymer was precipitated in a large excess of methanol. The polymer was recovered in 42% yield. IR (neat): C–H, 3000, 2960, 2875 cm^{-1} (s, s, s), Si–Me, 1265 cm^{-1} (s), Si–O–Si, 1065–1110 cm^{-1} (s), Ph–Si, 1180, 720, 700 cm^{-1} (m, m, m).

Table I
Molecular Weight and Glass Transition Temperatures of Poly(dimethylsiloxane-*co*-diphenylsiloxanes)

	diphenylsiloxane, mol %				
polymer	feed	copolymer	$10^{-5}\bar{M}_w$	T_g, °C	T_g,[a] °C
	Ring-Opening Polymerization				
1	52.9	54.8	1.15	-14	-49
2	35.9	44.8	0.91	-30	-79
3	27.2	33.7	1.50	-54	
4	19.9	30.8	2.08	-58	-105
5	8.6	9.3		-108	
	Condensation Polymerization				
6	50	53.4	2.56	-16	
7	50	29.6	1.94	...	
8	50	48.8	1.67	-9	

[a] Taken from ref 10.

Gel Permeation Chromatography. Gel permeation chromatograms were performed in duplicate on a Waters Model 200 GPC using THF at 30 °C. The samples were run through a series of Waters u-styragel GPC columns of mixed porosity and detected by using a ACS 750/14 mass detector. The molecular weights were calculated by using Hewlett-Packard HP-3388 with GPC (REV2048) programming.

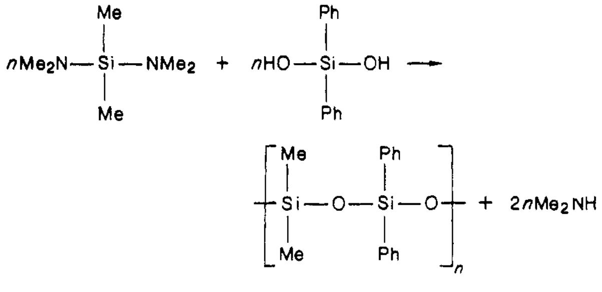
Infrared Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer infrared spectrophotometer (Model 283B). The films were cast from 5% (w/v) solutions in tetrahydrofuran. Casting was done directly on the sodium chloride plates, and after the evaporation of the solvent the films were dried.

Thermal Transitions. To determine the transition temperatures of the polymers a Perkin-Elmer DSC-4 with TADS was used. In all cases a temperature interval between −150 to 25 °C was covered at a heating rate of 20 °C/min. The samples analyzed ranged from 10 to 25 mg in weight, and a maximum sensitivity 2 mcal/s was used.

Results and Discussion

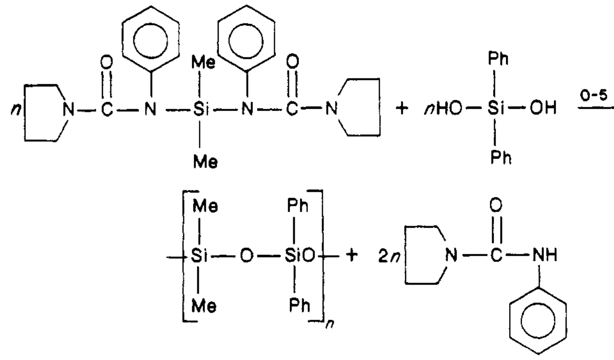
Ring-Opening Polymerization. The copolymerization of octamethylcyclotetrasiloxane (methyl tetramer, D_4) and octaphenylcyclotetrasiloxane (phenyl tetramer, D_4^{Ph}) was carried out at 165 °C by using KOH as an initiator. The feed ratios of monomers and the resultant copolymer compositions for the five copolymers 1–5 as determined from ^1H and ^{29}Si NMR are summarized in Table I. A perusal of the data show that the growing chains react preferentially with the phenyl tetramer as compared to methyl tetramer. Random copolymers are expected to be produced in view of the long equilibration times. The reaction rates seem to be governed by the dissolution of the phenyl tetramer in methyl tetramer, the electropositive character of the metal atom, the structure of the incoming monomer and the stability of siloxanolate anion. Our results are consistent with the earlier reported.[8,9] Copolymers rich in diphenylsiloxy units are opaque, suggesting the presence of some degree of crystallinity. DSC analysis, however, did not show a melting endotherm within the temperature range of 25–250 °C. High phenylsiloxy-containing material produced cloudy solutions in toluene suggesting short blocks of diphenylsiloxy units, which is confirmed by the NMR analysis (see below) which shows the greatest level of diphenylsiloxane triads in these samples.

Condensation Polymerization. In order to design ordered poly(dimethylsiloxane-*co*-diphenylsiloxanes), alternate synthetic approaches were conducted. Copolymer **6** was prepared by step-growth condensation via the reaction of diphenylsilanediol with bis(dimethylamino)dimethylsilane in toluene at 95–105 °C (eq 4). The above



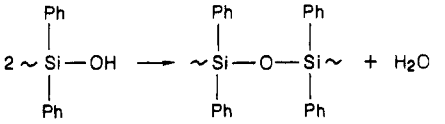
$$n\,\mathrm{Me_2N{-}\underset{Me}{\overset{Me}{Si}}{-}NMe_2} + n\,\mathrm{HO{-}\underset{Ph}{\overset{Ph}{Si}}{-}OH} \longrightarrow \left[\mathrm{\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Ph}{\overset{Ph}{Si}}{-}O}\right]_n + 2n\,\mathrm{Me_2NH} \qquad (4)$$

reaction did not produce the expected alternating polymer (see NMR analysis below) probably because the liberated base evolved in the bond-breaking process catalyzes randomization of the polymer through Si–O–Si bond rupture. The key to design an exactly alternating polymer, of course, lies in selecting reactants whose products would not invoke side reactions. Condensation reaction between diphenylsilanediol and bisureidosilane seems to meet the above requirement. Copolymer **8** was prepared according to reaction 5. This reaction is a nucleophilic substitution



(5)

on the ureidosilane by the silanol as the nucleophile, and with these reagents the reaction is rapid enough to proceed easily at low reaction temperatures of 0–5 °C. The byproduct urea is a neutral molecule and hence should not cause Si–O–Si bond rupture. The only possible side reaction is the silanol condensation. If such a reaction is possible, it would not only destroy the alternating character but also limit the molecular weight of the final product due to loss of stoichiometry of the reacting functional groups (eq 6). Water formed in this condensation could react



$$2\sim\mathrm{\underset{Ph}{\overset{Ph}{Si}}{-}OH} \longrightarrow \sim\mathrm{\underset{Ph}{\overset{Ph}{Si}}{-}O{-}\underset{Ph}{\overset{Ph}{Si}}}\sim + \mathrm{H_2O} \qquad (6)$$

with a ureidosilane monomer that can complicate the process further. However, the condensation reaction is unlikely to occur because the reaction takes place at subambient temperature. Further, the chlorobenzene used in the synthesis is a good solvent for the polymer and a non-solvent for the urea byproduct, which precipitated as the reaction progressed. This might provide an additional driving force for the completion of the condensation polymerization. Extreme care must be exercised to carry out the reaction under argon in order to avoid the reaction between moisture and ureidosilane. For comparison purposes copolymer **7** was also prepared by condensing 1,7-bis(dimethylamino)trisiloxane and diphenylsilanediol in toluene at 95–105 °C (eq 7).

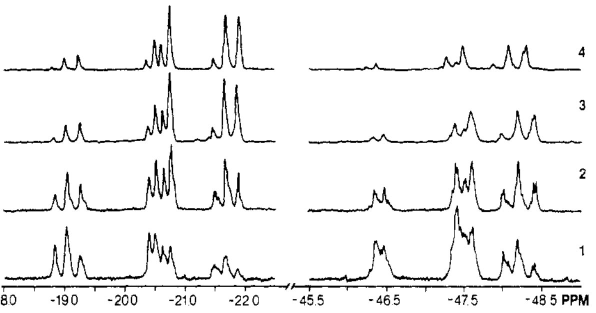


Figure 1. ^{29}Si NMR spectra of copolymers 1–4.

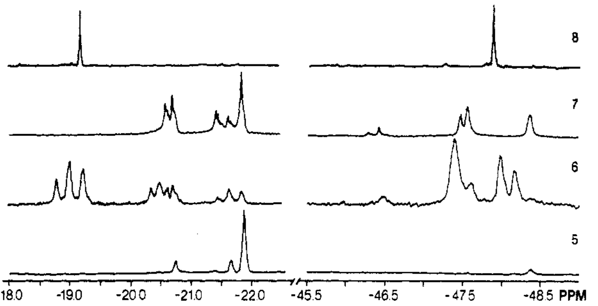
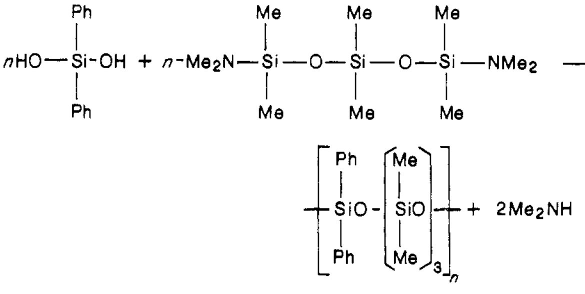


Figure 2. ^{29}Si NMR spectra of copolymers 5–8.

Chart I

I	$-SiPh_2O-\underline{SiMe_2O}-SiPh_2O-$
II	$-SiPh_2O-\underline{SiMe_2O}-SiMe_2O-$
III	$-SiMe_2O-\underline{SiMe_2O}-SiMe_2O-$



$$n\,\mathrm{HO{-}\underset{Ph}{\overset{Ph}{Si}}{-}OH} + n\text{-}\mathrm{Me_2N{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}NMe_2} \longrightarrow \left[\mathrm{\underset{Ph}{\overset{Ph}{Si}}O{-}\left(\underset{Me}{\overset{Me}{Si}}O\right)_3}\right]_n + 2\mathrm{Me_2NH} \qquad (7)$$

Gel Permeation Chromatography (GPC). Molecular weights and polydispersities of all polymers were evaluated by GPC. The weight average molecular weights of a copolymer, **1–5**, tend to decrease with increase in diphenylsiloxane content in the copolymer (Table I). It can be seen from these data that in all cases molecular weight distributions are characterized by polydispersities close to two.

Sequence Analysis. Sequence distribution studies have made significant advances to understanding the copolymerization mechanisms and the relationship between copolymer properties and chain microstructure.[14-16] NMR spectroscopy is well established as a valuable technique for determining the microstructure of polymers.[17] The sequence analysis to the pentad level of poly(dimethylsiloxane-*co*-diphenylsiloxanes) has been discussed previously.[18-20] ^{29}Si NMR spectra of copolymers **1–8** are shown in Figures 1 and 2. The ^{29}Si NMR spectra show two sets of major multiplets, one between −18 and −22 ppm for $SiMe_2O$ (referred to as M)[21] and one between −46 and −49 ppm for $SiPh_2O$ (referred to as P).

Considering first the triad sequence of the dimethylsiloxane, three multiplets are expected for the following three types of structures (Chart I). The ^{29}Si spectra (Figures 1 and 2) show three major multiplets for the

Chart II

Ia	$-SiPh_2O-SiPh_2O-\underline{Si}Me_2O-SiPh_2O-SiPh_2O-$
Ib	$-SiPh_2O-SiPh_2O-\underline{Si}Me_2O-SiPh_2O-SiMe_2O-$
Ic	$-SiMe_2O-SiPh_2O-\underline{Si}Me_2O-SiPh_2O-SiMe_2O-$
IIa	$-SiPh_2O-SiPh_2O-\underline{Si}Me_2O-SiMe_2O-SiPh_2O-$
IIb	$-SiMe_2O-SiPh_2O-\underline{Si}Me_2O-SiMe_2O-SiPh_2O-$
IIc	$-SiPh_2O-SiPh_2O-\underline{Si}Me_2O-SiMe_2O-SiMe_2O-$
IId	$-SiMe_2O-SiPh_2O-\underline{Si}Me_2O-SiMe_2O-SiMe_2O-$
IIIa	$-SiPh_2O-SiMe_2O-\underline{Si}Me_2O-SiMe_2O-SiPh_2O-$
IIIb	$-SiPh_2O-SiMe_2O-\underline{Si}Me_2O-SiMe_2O-SiMe_2O-$
IIIc	$-SiMe_2O-SiMe_2O-\underline{Si}Me_2O-SiMe_2O-SiMe_2O-$

$SiMe_2O$ which are clearly attributed to the above three structures. Additional splitting is attributed to the possible pentad sequences shown in Chart II.

In a 50:50 random copolymer, the multiplets due to triads I and III should become 1:2:1 triplets when pentads are considered since sequences Ib and IIIb are degenerate, and there is equal probability for the reverse sequences. However, the pentads from II become a 1:1:1:1 quartet because IIb and IIc are not symmetric structures. (Previous authors have not noted the inequivalence of IIb and IIc in their analyses.)

The dimethylsiloxane portion of the ^{29}Si spectra of **1** and **2** shows two 1:2:1 multiplets and a 1:1:1:1 multiplet which, based on the above analysis, are assigned to I, III, and II sequences, respectively. The upfield peak of the upfield multiplet is assigned to IIIc on the basis of the similarity of its chemical shift to that of polydimethylsiloxane homopolymer, −22.2 ppm.[22] The assignment of this peak to IIIc is confirmed by noting that this peak is the strongest resonance in the spectrum of **5**, which is over 90% M units and must contain appreciable levels of block polydimethylsiloxane units IIIc. The chemical shifts of the other peaks are then assigned to sequences assuming that each replacement of a dimethylsiloxane by a diphenylsiloxane causes a comparable downfield shift. Thus, the middle multiplet is assigned to $SiMe_2O$ between $SiPh_2O$ and $SiMe_2O$ (type II units), and the downfield multiplet is assigned to $SiMe_2O$ between two $SiPh_2O$ (type III units). The pentad sequence analysis proceeds via similar reasoning, but within one of the triad multiplets. Since the $SiPh_2O$ are now four bonds from the Si of interest, the effect of replacing $SiMe_2O$ by $SiPh_2O$ is much less. To first order, the chemical shifts of IIb and IIc should be the same since both sequences have 1α and 1β $SiPh_2O$ substituent on the $SiMe_2O$. These two absorptions are clearly distinguishable in the spectra (Figures 1 and 2); the assignment of IIb and IIc requires comparison of the $SiMe_2O$ pentad intensities with the $SiPh_2O$ triad intensities and is described below. The chemical shift assignment for the $SiMe_2O$ resonances are included in Table II. The ratios of the ten $SiMe_2O$ pentad absorptions were calculated by assuming Bernoullian trial statistics using the $\underline{Si}Me_2O$:$\underline{Si}Ph_2O$ ratio observed in the ^{29}Si NMR spectra (Table II). The calculated ratios are very similar to the observed ratios and confirm that the condensation polymers are random.

The dimethylsiloxane portion of the spectra of **1**–**7** show considerably more resolution than observed in the spectrum of a 70:30 dimethylsiloxane:diphenylsiloxane sample published by McGrath et al.[20] The improved dispersion is probably attributable to the use of a higher magnetic field in the present work.

Similar splittings to those seen for the dimethylsiloxane are expected for the diphenylsiloxane absorptions. The triad and pentad assignments are expected to be similar since the deshielding by $SiPh_2O$ should be comparable in both cases (Chart III).

Chart III

	Triads
IV	$-SiPh_2O-\underline{Si}Ph_2O-SiPh_2O-$
V	$-SiPh_2O-\underline{Si}Ph_2O-SiMe_2O-$
VI	$-SiMe_2O-\underline{Si}Ph_2O-SiMe_2O-$
	Pentads
IVa	$-SiPh_2O-SiPh_2O-\underline{Si}Ph_2O-SiPh_2O-SiPh_2O-$
IVb	$-SiPh_2O-SiPh_2O-\underline{Si}Ph_2O-SiPh_2O-SiMe_2O-$
IVc	$-SiMe_2O-SiPh_2O-\underline{Si}Ph_2O-SiPh_2O-SiMe_2O-$
Va	$-SiPh_2O-SiPh_2O-\underline{Si}Ph_2O-SiMe_2O-SiPh_2O-$
Vb	$-SiMe_2O-SiPh_2O-\underline{Si}Ph_2O-SiMe_2O-SiPh_2O-$
Vc	$-SiPh_2O-SiPh_2O-\underline{Si}Ph_2O-SiMe_2O-SiMe_2O-$
Vd	$-SiMe_2O-SiPh_2O-\underline{Si}Ph_2O-SiMe_2O-SiMe_2O-$
VIa	$-SiPh_2O-SiMe_2O-\underline{Si}Ph_2O-SiMe_2O-SiPh_2O-$
VIb	$-SiPh_2O-SiMe_2O-\underline{Si}Ph_2O-SiMe_2O-SiMe_2O-$
VIc	$-SiMe_2O-SiMe_2O-\underline{Si}Ph_2O-SiMe_2O-SiMe_2O-$

However, as seen in Figures 1 and 2, the $SiPh_2O$ portion of the spectrum does not show the expected set of 10 peaks. Polymers **1** to **5** are random copolymers containing decreasing amounts of $SiPh_2O$. The increase in the relative intensities of the upfield $SiPh_2O$ multiplet in this series indicates the upfield multiplet must be assigned to triad VI. This assignment is confirmed by polymer **8** in which the only significant peaks are alternating pentad sequences Ic and VIa. The general line broadening of the diphenylsiloxy resonances in all copolymers is probably caused by a combination of the anisotropy of the phenyl ring and aromatic ring association. PP dyad associated interactions also explain the greater apparent intensity of IIb relative to IIc even though they must have identical intensities in Bernoullian polymers **1**–**5**. Since these peaks do not show base-line resolution, broadening of IIc with the PP dyad would systematically lower its observed intensity. The presence of PPP triads and PPPP tetrads in the IV and V pentads further degrades the observable resolution due to long range conformational effects.

Although three distinct regions are observed for the P-centered triads, the pentad sequences IV and V are overlapped in the copolymers **1**–**6**. However, copolymers **1**–**6** showed well-resolved peaks due to MPM centered pentads. Long-range sequences (heptads) are also evident from the spectra of **1** and **2**. The probable chemical shift assignments for P-centered pentads are given in Table II. Excellent agreement is observed between the calculated and observed intensities of the MPM-centered pentads. The resolution is insufficient to compare the calculated and observed intensities for the PPP and MPP pentads.

The triad $SiPh_2O$ assignment is confirmed, and the pentad $SiMe_2O$ assignment unambiguously made by calculating the $SiPh_2O$ triad intensities directly from the $SiMe_2O$ pentad intensities (Table III). This calculation is possible since the phenyl next to the center $SiMe_2O$ is uniquely assignable in the $SiMe_2O$ pentads. The intensities of type V and type VI triads are given by eq 8 and 9, where $A(\mathrm{M})$ is the intensity of triad or pentad M.

$$A(\mathrm{V}) = A(\mathrm{Ib}) + A(\mathrm{IIa}) + A(\mathrm{IIc}) + 2A(\mathrm{Ia}) \qquad (8)$$

$$A(\mathrm{VI}) = {}^1/_2A(\mathrm{Ib}) + {}^1/_2A(\mathrm{IIb}) + {}^1/_2A(\mathrm{IId}) + A(\mathrm{Ic}) \qquad (9)$$

The factors of $^1/_2$ arise in eq 9 because the P's in MPM triads are counted twice. The intensity of triad IV, block $SiPh_2O$ units, is determined by difference since the total $SiPh_2O$ level is known from the integration of the $SiMe_2O$ region relative to the $SiPh_2O$ region. There is excellent agreement between the calculated and observed triads for all copolymers rich in $SiPh_2O$ content. The poor correspondence between the calculated and observed level of

Table II
Calculated (Bernoullian Statistics) and Observed (^{29}Si NMR) Pentad Peak Intensities

		polymer															
		1		2		3		4		5		6		7		8	
		obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
								$SiMe_2O$–									
−18.78	Ia	8	9	4	4	1	1	1	1	0	0	12	9	0	1	0	8
−19.00	Ib	16	15	10	9	5	5	4	4	0	0	22	14	0	3	7	14
−19.21	Ic	8	6	7	6	6	5	5	5	1	1	18	6	0	4	80	6
−20.34	IIa	14	15	9	9	9	5	5	3	4	0	0	8	14	3	0	14
−20.45	IIb	14	12	13	12	11	10	9	9	2	1	9	12	4	8	2	12
−20.58	IIc	11	12	11	12	9	10	8	9	2	1	5	12	20	8	0	12
−20.71	IId	11	10	16	16	21	20	22	20	11	14	9	10	16	21	3	11
−21.43	IIIa	6	6	6	6	5	5	4	5	3	1	4	6	19	4	0	6
−21.63	IIIb	8	10	14	16	18	20	21	20	15	14	6	10	13	21	2	11
−21.85	IIIc	3	4	10	10	19	19	23	23	67	67	6	4	26	26	5	5
								$SiPh_2O$–									
−46.30	IVa	25	9	16	4	0	1	0	1	0	0	0	9	0	1	0	8
−46.39	IVb		15		9	3	5	3	4	0	0	0	14	6	3	0	14
−46.55	IVc		6		6	5	5	4	5	0	1	6	6	8	4	0	6
−47.12	Va	51	15	20	9	14	5	12	4	0	0	55	14	0	3	0	14
−47.33	Vb		12		12		10		9	0	1		12	4	8	6	12
−47.46	Vc		12	11	12	7	10	5	9	3	1		12	22	8	0	12
−47.54	Vd		10	17	16	21	20	23	20	12	14		10	28	21	0	11
−47.96	VIa	8	6	8	6	7	5	6	5	3	1	24	6	2	4	84	6
−48.13	VIb	12	10	17	16	23	20	23	20	18	14	12	10	3	21	8	11
−48.33	VIc	4	4	10	10	21	19	25	23	63	67	4	4	26	26	2	5

Table III
Comparison of Observed $SiPh_2O$ Triads and Triads Calculated from $SiMe_2O$ Pentads

	polymer															
	1		2		3		4		5		6		7		8	
	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
IV	25	27	16	18	8	13	7	13	0	13	6	17	13	18	0	15
V	51	48	49	47	42	40	40	37	15	21	55	51	55	57	6	7
VI	24	25	35	34	50	47	53	50	85	67	39	32	32	25	94	78
	Triad Intensities, Calculated with Opposite Assignment of IIb and IIc															
IV	25	26	16	17	8	12	7	12	0	15	6	15	13	39	0	14
V	51	51	49	50	42	43	40	39	15	16	55	54	55	16	6	8
VI	24	23	35	33	50	46	53	49	85	69	39	30	32	45	94	77

triad IV and polymers **5**, **7**, and **8** occurs because it is determined as a small difference between two large numbers.

Polymer **7** provides unambiguous assignments of the IIb and IIc pentads. The calculated $SiPh_2O$ triads from $SiMe_2O$ pentads with and without inverting the IIb and IIc pentad assignment are given in Table III. There is excellent agreement between the observed and calculated $SiPh_2O$ triads for the IIb/IIc assignment given above, whereas the reverse assignment gives unreasonable values for triads V and VI. Although similar calculations can be extended to Vb and Vc, peak overlap in the $SiPh_2O$ resonance region limits realistic calculations of $SiMe_2O$ triads from $SiPh_2O$ pentads. Calculations for **5** and **7** do not distinguish Vb and Vc within experimental error in the triad sequences of I and III because these samples are over 75% M.

Analysis of condensation copolymers **6**, **7**, and **8** is very informative. Polymer **6** exhibits about 20% Ic and VIa sequences, indicating the sample is 40% alternating. Deleting Ic and VIa and part of Ib and VIb pentads, the majority of the remaining sequences have intensities in accordance with the random distribution applicable to Bernoullian trial statistics. This random order may be due to one or both of the following: (i) silanol condensation, (ii) randomness caused by the liberated base dimethylamine. The former reaction is highly probable as the reaction was conducted at elevated temperatures. The water produced, in situ, from silanol condensation may further rupture Si–N bonds of the aminosilane monomer leading to various random sequences. Presence of a low concentration of IIIc sequence supports the possible Si–N bond cleavage.

Polymer **7** should have the sequence PMMMPMMMP. All the P-centered pentads should be in VIc pentads whereas the M-centered pentads should show a 2:1 ratio of IIIa:IId. The observed intensities confirm high populations for these three pentads, but also show high levels of pentads IIc, Vc, and Vd, indicating high level of PP dyads. Presence of these PP dyads originates from the same reactions explained for polymer **6**. Although this sample contains only 29% diphenylsiloxy, over 14% of the $SiPh_2O$ groups are in tetrad or pentad blocks (sequences IVa and IVb).

Polymer **8**, as expected, is an alternating polymer with greater than 90% alternating sequences. The NMR analysis, however, indicates a significant level (10%) of the units is in other sequences that may be due to side reactions occurring during synthesis.

Thermal Transitions. The DSC scan of the polydimethylsiloxane (PDMS) shows a glass transition T_g at −123 °C, a crystallization exotherm (T_m) at −78 °C, and a melting endotherm (T_m) at −45 °C. All three of these transitions have been observed and reported in the literature.[21] The DSC scans of all copolymers exhibit only one second-order phase transition. No crystallinity is detected in all the polymers. The presence of as little as 3% diphenylsiloxane content in the copolymer has been shown

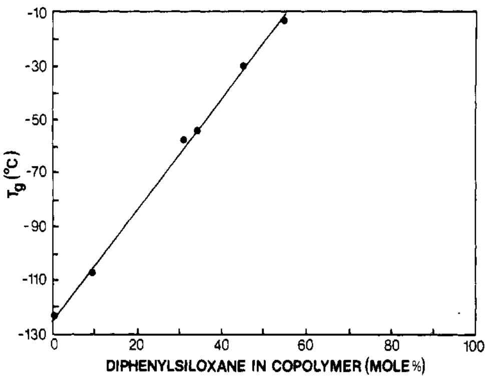


Figure 3. A graph of T_g of poly(dimethylsiloxane-*co*-diphenylsiloxanes) as a function of composition.

to disrupt the crystallinity.[23] Reported data show that the chain length of the polymer[24] and the terminal functional groups could affect the T_g of a polymer.[25] Cowie and McEwen[24] have shown that the glass transition temperatures of a series of PDMS fractions increase with increasing molecular weights. For pure linear PDMS samples of M_n = 540 and 1200, the reported values are −137 and −130 °C, respectively. At M_n above 4200 T_g reaches a limiting value of −124 °C. The T_g of PDMS determined from our experiments is consistent with the data reported by Cowie and McEwen. Similar data were obtained by Krause et al.[26] and Adachi et al.[27] McGrath et al.[10] showed the T_g of low molecular weight ($M_n \approx 2000$) amino functional PDMS at −123 °C. This is in contradiction to the data shown by Cowie and McEwen for low molecular weight polysiloxanes. In addition to this, these values suggest that the polar terminal aminopropyl groups have no effect on the T_g of the polymers. Recently Cameron and Chisholm[25] reported that the terminal methacrylate groups in low molecular weight PDMS significantly increase the T_g of the polymer. They have also further shown that for higher molecular weight PDMS macromers ($M_n \approx 25000$) the T_g's are close to those of PDMS. The glass transition temperatures of copolymers increased with increase in $SiPh_2O$ content (Table I). The T_g of poly(dimethylsiloxane-*co*-diphenylsiloxanes) as a function of composition is presented graphically in Figure 3. The data clearly demonstrate that $SiMe_2O$ and $SiPh_2O$ units are randomly distributed along the polymer chain. The T_g data of some of the copolymers with nearly the same composition as those reported by McGrath et al. for functional oligomeric copolymers are presented in Table I for comparison purposes. It is not clear whether these discrepancies are a result of differences in molecular weights, terminal functional groups, sequence distribution, or a combination of all three. Since the reported T_g of PDMS is identical with our values, the data reported by McGrath et al. are questionable. Comparing **1** and **6** indicates that the sequence distribution does not seem to change significantly the T_g values. It is, however, noteworthy to mention that the alternating polymer **8** showed a T_g at −9 °C which is about 7 °C higher than the random copolymer of similar composition. This shows that the T_g of these copolymers is determined not only by how much of each monomer is in the chain but also by the arrangement of units in the chain.

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Registry No. **6**, 110205-41-9; **7**, 110205-42-0; **8**, 110205-43-1; bis(pyrrolidinyl)dimethylsilane, 64191-88-4; dimethyldichlorosilane, 75-78-5; pyrrolidine, 123-75-1; diureidosilane, 62725-50-2; phenyl isocyanate, 103-71-9; (octamethylcyclotetrasiloxane)(octaphenylcyclotetrasiloxane) (copolymer), 27881-19-2.

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