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Silicone Networks Prepared via a Living Percolation Mechanism: Postgelation Structure for Networks with a Variety of Junction Functionalities

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Abstract: Silicone networks were prepared by the trifluoromethanesulfonic-acid-catalyzed polymerization of octamethylcyclotetrasiloxane and an oligocyclosiloxane. The polymerization occurred by the random exchange of all siloxane bonds in the sol and the gel. Networks where the junctions were tri-, tetra-, penta-, hexa-, hepta-, or octafunctional were prepared. The final structure was modeled by a simple thermodynamic consideration of the ring–chain equilibrium involved. The sol was primarily composed of cyclic oligomers of dimethylsiloxane which were in equilibrium with the network. The composition of the various sized rings was analyzed to verify the structure assigned to the network. Equilibrium swelling studies were carried out which strongly supported the calculated structures. A correlation between the average functionality and cycle rank of nearly perfect lightly cross-linked networks is given.

Introduction

Virtually all elastomeric networks are prepared by one of three methods.[1] The first is the step-growth condensation or addition of a mixture of difunctional and polyfunctional monomers, as in the preparation of poly(urethane)- or poly(ester)-cured resins. The second method is to chain copolymerize a vinyl monomer with a divinyl monomer, as in the preparation of a network from styrene and divinylbenzene. The third method is the coupling of two modified polymers or of a modified polymer with a small polyfunctional reagent. This method includes radiation-induced and peroxide-induced free-radical cross-linking of polydimethylsiloxanes as well as the common room-temperature vulcanization and hydrosilation curing of polydimethylsiloxanes.

These methods all proceed via a series of essentially irreversible reactions between a pair of complimentary functionalities. Many, such as radical curing, display a number of side reactions which are not easily controlled. The structure that forms can be modeled only if the appropriate rate and equilibrium constants are known for the reactions between the various monomers and functionalized polymers which are formed. After the gel point, diffusion processes become a dominant factor in determining the extent and selectivity of the intramolecular reactions of the gel and the intermolecular reactions with the sol which lead to the final network structure. Long-range diffusion of functionality attached to the network lattice does not occur and limits the attainable extent of reaction. Though in some cases the extent of reaction can be determined spectroscopically,[2] typically the distribution, the number, and the functionalities of the cross-linking junctions are assigned on the basis of assumptions of selectivity and conversion or by the physical or mechanical properties exhibited by the network.[3] This practice has been considered necessary, with the unfortunate consequence of leaving many discrepancies between measured and theorized properties which could not be definitively attributed to either the weaknesses in the theory or the ambiguities of the defined network structure.

Most model networks have been silicones because they display an extremely low glass transition temperature and do not tend to form crystalline segments at high elongations.[4] The "best" model networks to date have been formed by hydrosilation curing between α,ω-divinylpolydimethylsiloxanes with polyfunctional, usually tetrafunctional, silanes or siloxanes of the complimentary Si–H functionality or by condensation of tri- and tetraalkoxysilanes with α,ω-dihydroxypolydimethylsiloxanes.[3,5] In these cases, the stoichiometry of the end-capped polymer and the polyfunctional monomer and the occurrence of any chain-end imperfections must be well known. To achieve reproducible network formation, the polymer chains that have been used in these studies generally have molecular weights below 20 000. Typically, it is assumed that all nonextractable functionality has undergone reaction, that the number average degree of polymerization and molecular weight distribution between cross-links is the same as that of the polymer prior to cross-linking, and that the functionality of all junctions is that of the polyfunctional reagent. Many of the discrepancies between observed and calculated network properties have been attributed to undetermined quantities of imperfections such as dangling chains and defective, lower functionality junctions.[6] Often the formation of physical cross-links due to entanglements of the polymer chains prior to cross-linking[6,7] or the unpredictable formation of ineffective loops[2,6,8,9] has been suggested as the reason for difficulties in correlating the network topology to the observed properties.

Simulations of the cross-linking of poly(dimethylsiloxane)[9] and poly(isoprene)[10] by the random joining of repeating units, as in

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1993.

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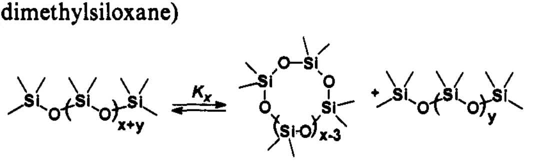
a radiation cure, and for the reaction of a telechelic poly(dimethylsiloxane) with tri-[11] or tetrafunctional[12] cross-linkers have been carried out. These simulations indicated that a significant amount of cyclic defects form, with the smaller possible rings predominating. They have shown that the actual topology will depend strongly on the extent of the cross-linking reaction and on the stoichiometry of a telechelic polymer to the cross-linking molecule. These models qualitatively describe the types of defects that form and gave reasonably good quantitative predictions of gel points;[13] the correlation of model network properties to topology suffers from the difficulty in determining the degree of cross-linking after gelation. In all cases, assumptions were made about the selectivity and completeness of the cross-linking reactions to assign the topology, and it has been pointed out that the models are "limited by a lack of comprehensive understanding of all reaction rates and routes".[9]

Though advances in analytical methods may eventually permit the full characterization of the structure of a rubber network prepared by these methods, a network synthesis which permits the assignment of the final structure from thermodynamic considerations rather than from assumptions about postgelation kinetics should permit the formation of superior model networks. Such a structure could be predicted from statistical considerations. Additionally, it would be advantageous to have a method of determining when the minimum structure is achieved, as the reorganization would involve a mechanism whose rate could not necessarily be predicted after gelation. Such a system would involve the reversible formation of chain elements of the network and the sol in a manner that permits the system to reorganize itself until the thermodynamic minimum structure is formed and could be verified by the achievement of the statistically predicted sol composition that would be distinctly different from the sol composition prior to equilibrium.

This research group has chosen to explore the synthesis of model networks by the ring-opening copolymerization of octamethylcyclotetrasiloxane and oligocyclodimethylsiloxanes to take advantage of the nature of the polymerization mechanism. The polymerization proceeds to equilibrium and displays living behavior[14] using either an acid[15,16] or base[15,17] catalyst. Polymerization of unstrained cyclosiloxanes such as octamethylcyclotetrasiloxane is accompanied by depolymerization and chain transfer to the polymer, resulting in a mixture of linear and cyclic homologues which is formed in a completely random manner (Scheme I). The final molecular weight and molecular weight distribution can be predicted from a knowledge of the starting composition and the equilibrium constants for cyclization. The cyclic equilibrium constants have been measured by a number of research groups.[18] Silicone copolymers have been shown to display a random placement of the repeating units by an analysis of the equilibrium cyclo–cosiloxane composition.[19] Typically, the molecular weight is controlled by the addition of a disiloxane, such as hexamethyldisiloxane, to give a trialkylsilyl end-capped polymer which has an equilibrium number average degree of polymerization equal to the moles of dimethylsiloxane groups which do not reside in cyclosiloxanes divided by the moles of disiloxane used.[20] Although the relative rate at which dimethylsiloxy and trialkylsiloxy units are incorporated into the polymer depends upon the catalyst,[15] the final equilibrium molecular weight distribution is a Flory–Schultz distribution[21] and the final cyclic distribution is similar to that predicted by Jacobson–Stockmeyer theory.[22]

Scheme I. Ring-Chain Equilibrium in Living Poly(dimethylsiloxane)



The copolymerization approach to silicone rubbers was first investigated more than 3 decades ago.[23] This study was carried out prior to the first determination of the equilibrium constants for cyclosiloxanes by Brown and Slusarczuk.[18c] Perhaps for that reason, there was no reported characterization or assignment of the resulting network structure, and the investigation focused on the catalysts used to prepare these networks. Since those publications, a number of significant advances in redistribution catalysis and Si–C bond-forming reactions have been realized. Although a number of oligocyclosiloxane compounds that are appropriate for such studies have been reported,[24] no attempts to characterize such networks have been reported.[25]

This paper describes the networks prepared by the copolymerizations of a series of oligocyclosiloxanes with octamethylcyclotetrasiloxane. The oligocyclosiloxanes consisted of silicon atoms connected via ethylene bridges (Figure 1). All Si–O bonds of the polyfunctional core of these oligocyclics can be considered as part of either a dialkylsiloxy or trialkylsiloxy unit; hence, the placement of the different groups in the equilibrium network should be similar to that observed in linear polymerization systems. Since chain–chain and ring–chain equilibriums occur, the active centers for polymerization can percolate throughout the network via the exchange of nearest neighbor chain-link elements (Figure 2), since all Si–O bonds are reactive sites. In this way, only short-range diffusion is necessary to achieve the equilibrium structure. The junction's functionality depended upon the number of Si–O bonds which were connected via the ethylene bridges which do not cleave under the polymerization conditions. If the junctions are distributed randomly in the network as comonomers and end cappers are distributed randomly in linear polymers, then a normal distribution of chain lengths between junctions

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(14) The active center does not terminate under the polymerization conditions; however, chain transfer occurs, unlike what are traditionally considered as living polymers (see: Szwarc, M. *Nature* **1956**, *178*, 1168). A narrow molecular weight distribution can result only because a network is formed.

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(25) Two patents have been issued where biscyclosiloxanes have at least one cyclic being the cyclic trimer for the preparation of elastomers. (a) Nitzche, S.; Burkhardt, J.; Wegehaupt, K.-H. U.S. Patent 3,629,359, Dec 21, 1971. (b) Nitzche, S.; Burkhardt, J.; Wegehaupt, K.-H. U.S. Patent 3,706,591, Dec 21, 1971. One patent has described the use of bis(heptamethylcyclotetrasiloxanyl) end-capped imides for the preparation of resins. (c) Buese, M. A. U.S. Patent 4,826,710, May 2, 1989. Only a qualitative description of the networks was given in all cases.

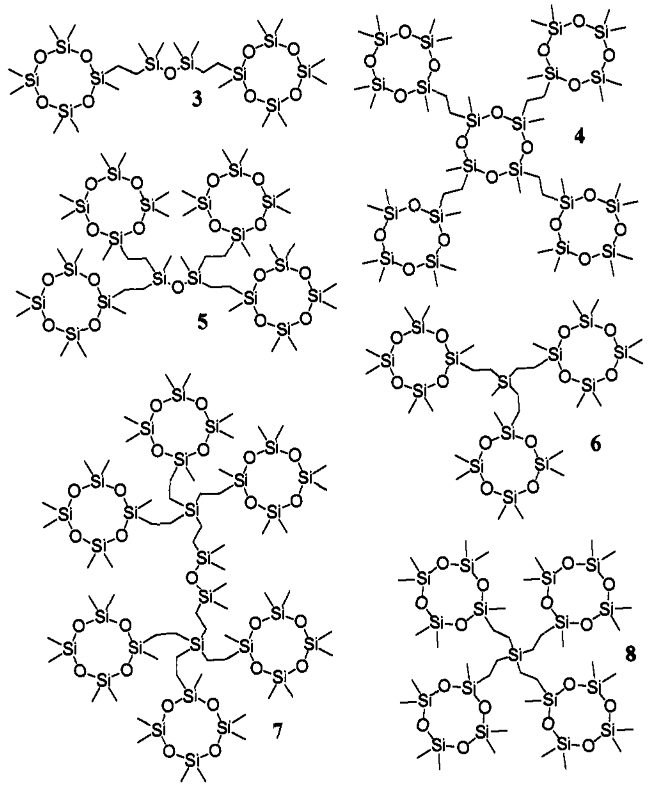

Figure 1. Oligocyclodimethylsiloxanes used for the preparation of networks where the compound number is also the maximum junction functionality *f* imparted to the model network.

will result. The similarity between chains connected by network junctions and free linear chains has been demonstrated by SANS experiments.[26]

All junctions do not have their maximum functionality, which is determined by the number of Si–O linked via Si–C and C–C bonds. The junctions have defects as in previously prepared model siloxanes; however, the structure and number of these defects can be assigned since they arise from cyclic formation. These cyclic defective junctions are in equilibrium with the network and the sol, which is composed primarily of cyclodimethylsiloxanes. Hence, the structure of the network, the number and structure of the junction defects, the chain length between branch junctions, and the amount and composition of the sol can be predicted at equilibrium. The composition of the sol can be analyzed, and in principle, this composition can verify the achievement of equilibrium.

In addition to the description of the preparation and characterization of networks prepared by the trifluoromethanesulfonic-acid-catalyzed polymerization of octamethylcyclotetrasiloxane and oligocyclosiloxanes, a simple statistical model is described which considers only the first level of connectivity of junctions for the assignment of the structure after termination of the catalyst. Chain ends resulting from reactions with the catalyst and the different types of cyclic structures that could form were considered and experimentally investigated. For some networks, an analysis of the sol was carried out which supported the structural assignment of the networks that were prepared. Equilibrium swelling results are also presented. They suggest that the topology was reasonably assigned by the model when the maximum functionality of the junctions was four or greater. The relationship between the average functionality and cycle rank of a nearly perfect lightly cross-linked network is described.

Results and Discussion

Potential Structural Defects. To assign the network structure and the sol composition, the proportion of the monofunctional, difunctional, and polyfunctional units in the network and its equilibium sol must be known. The true functionality of the junctions must also be known. All junctions should not be assigned the functionality that they would posses if all of their potential sites of attachment to the network are ends of active chains, which has been frequently done for model networks. The distribution of these various units must also be known. In order to assign the proportion and connectivity of these units to the networks, one must first consider the possible structures that can form upon reaction of the junction units, the dimethylsiloxy units, and the acid. The dimethylsiloxy units will be distributed randomly between cross-linked units and chain ends and in cyclosiloxanes. Potential sources of chain ends are acidolysis products and defective junctions. The defective junctions are those which contain cyclic structures. Two types of cyclic structures which incorporate two junction sites are possible. Cyclosiloxanes constitute the more numerous type of junction defects, where a single dimethylsiloxy-like unit of a junction or two or more of these units from different junctions are included in the ring as shown in Figure 3. The proportion of rings which contain one, two, or more junctions depends upon the ratio of dimethylsiloxy units to junction units in the system, but the proportion of junction sites incorporated into cyclics should be nearly invariant with the composition. Cycloparaffinsiloxanes, where two siloxy units from a single junction combine with or without (Figure 4) additional siloxy groups, comprise the other possible junction defects. The concentration of cycloparaffinsiloxanes should decrease as the number of junctions in the system decreases.

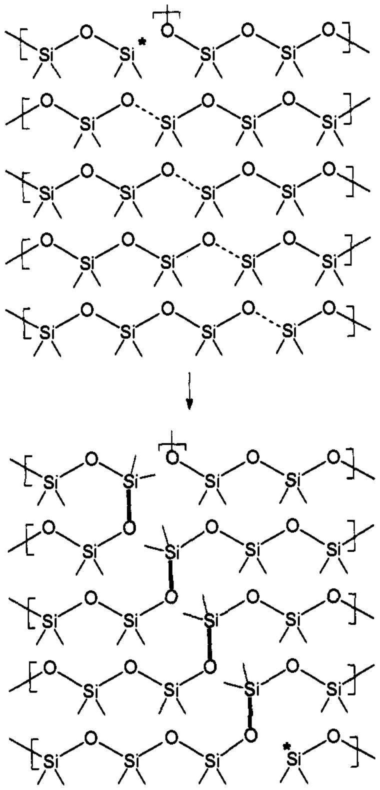

Figure 2. Percolation of an active center (marked with an asterisk) from the upper left to the lower right, where bonds to be broken are indicated in the upper structure by dashed lines and bonds that were formed are indicated by bold lines in the lower structure.

The structures formed from the reaction of trifluoromethanesulfonic acid with siloxanes have not been completely characterized. All studies of the polymerization of cyclosiloxanes with this acid indicate that acid and siloxane are in equilibrium with silyl ester and silanol, which is in equilibrium with siloxane and water.[27] There are no reported equilibrium constants for these processes in solvent-free systems. However, it is the quantity of monofunctional structures present after the catalytic activity is

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(26) Beltzung, M.; Picot, C.; Herz, J. *Macromolecules* **1982**, *15*, 1594.

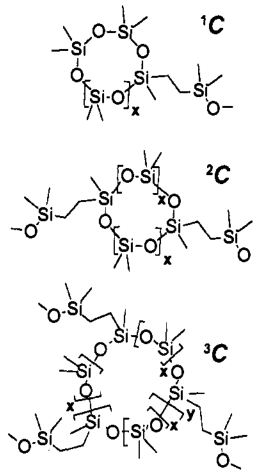


Figure 3. Three types of cyclosiloxanes containing D^J units considered in structural calculations, as illustrated with D^J units from **3**.

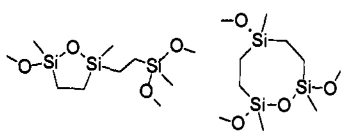


Figure 4. Five-membered (left) and eight-membered (right) cycloparaffinsiloxane structures that are possible upon redistribution of the Si–O bonds of **5**.

destroyed by reaction with MgO which is required for structural assignment. The percolation mechanism permits migration of the active centers to the rubber surface for termination. The mode of trifluoromethanesulfonic acid quenching by MgO is presently unreported in the literature; however, in addition to the acid–base reaction, the literature describes the use of MgO to couple silyl chlorides and other acid equivalents to form siloxanes.[28] As long as acid-catalyzed silanol condensation occurs at a competitive rate to the quenching reaction, all monofunctional units resulting from acidolysis should migrate to the surface and be consumed with the coupling of chains or with fixation of the end groups at the rubber surface. In that case, no monofunctional units which resulted from acidolysis should remain in the network.

To support that quenching occurs without the generation of monofunctional chain ends, a linear siloxane fluid was prepared by the redistribution of octamethylcyclotetrasiloxane and hexamethyldisiloxane such that the ratio of dimethylsiloxy to trimethylsiloxy units was 300. After equilibrium was established in the fluids, as indicated by a gas chromatographic analysis of the composition of cyclosiloxanes, the reaction was quenched with MgO and the viscosities of the fluid were determined at three different temperatures. The fluids were then reactivated by the addition of trifluoromethanesulfonic acid, and the viscosities of the "living" fluids were measured and the reaction again quenched. The viscosities of the twice-quenched fluid were found to be virtually identical to those after the first quench, as seen in Table I. This result indicated that the networks should not contain a discernible number of chain ends formed from the acid.

Table I. Observed Viscosity of an Equilibrium Fluid at Various Temperatures

sample no.	[HTrif] × 10^3 [a]	observed viscosity (cSt)		
		40 °C	70 °C	100 °C
1	0.0	3330	2160	1410
2	3.3	2790	1580	8810
3	0.0[b]	3340	2160	1400

[a] Concentration in moles/L. [b] Catalyst was deactivated by MgO after sample #2 was measured.

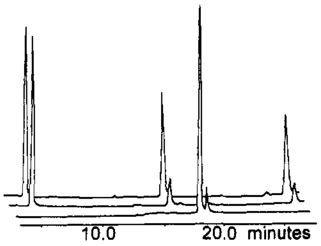
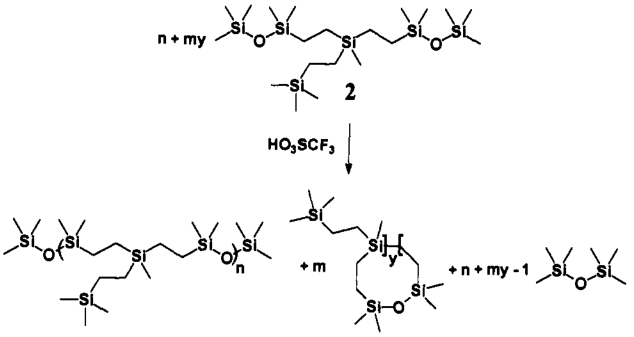
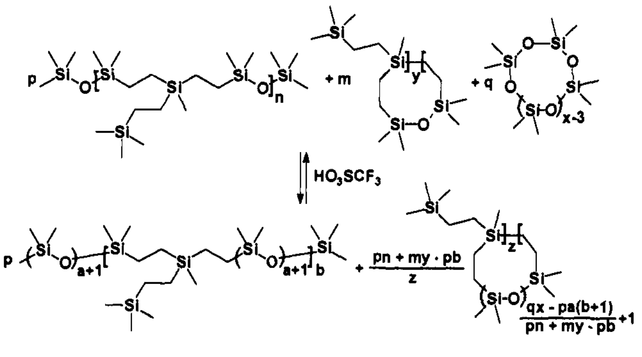


Figure 5. Gas chromatography traces of **2** (bottom), where the second small peak is due to an isomer resulting from β-Si addition of H during the hydrosilation reactions, and the cyclic monomer (16.5 min) and cyclic dimer (27 min) in equilibrium with the polymer from **2** in bulk (middle) and in solution (top) relative to the internal standard nanane (5.2 min).

Scheme II. Self-Condensation Polymerization of **2**



Scheme III. Redistribution of Octamethylcyclotetrasiloxane with the Polymer from **2**



Appreciable monomeric cycloparaffinsiloxane formation would not be anticipated in networks prepared from oligocyclics **3**–**5** (Figure 1) due to the formation of a five-membered ring (Figure 4) since the ring would be strained by more than 30 kJ/mol, as has been observed in the polymerization of the linear analogue 2,2,5,5-tetramethyl-2,5-disilaoxacyclopentane.[29] To investigate the potential for formation of eight-membered-ring cycloparaffinsiloxanes from oligocyclics **5**–**8** (Figure 1) or larger rings with the incorporation of dimethylsiloxy units, the equilibrium cyclic composition was determined for the polymer that resulted from the self-condensation of bis[2-((trimethylsiloxy)dimethylsilyl)ethyl]-(2-(trimethylsilyl)ethyl)methylsilane (**2**) (Scheme II), which is a linear analogue model for junctions from oligocyclics **5**–**8**, and its subsequent redistribution with various ratios of octamethylcyclotetrasiloxane (Scheme III). As was evident from analyses by gas chromatography (Figure 5) and ^{1}H NMR spectroscopy (Figure 6), although **2** was primarily the structure displayed in Schemes II and III, it consisted of a mixture of isomers, as were the oligocyclosiloxanes used in this study,[30] due

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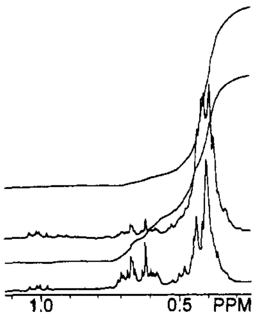
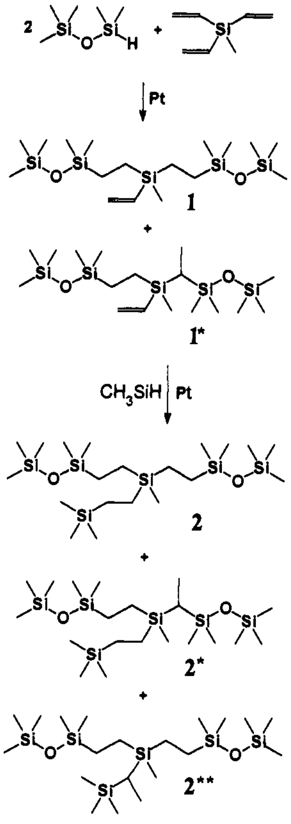


Figure 6. Portion of the ^{1}H NMR spectra of the polymer from **2** which displays two doublets for the two isomeric methyl groups resulting from β-Si addition of H during the hydrosilation reactions at 1.0 ppm and multiplets for the methylene groups of the polymer (0.4 ppm) and cyclic monomer (0.63 ppm) observed by redistribution of **2** in bulk (top) and in solution (bottom).

Scheme IV. Preparation of **1** and **2** by Hydrosilation Showing the Major Isomers That Were Formed Due to α-Si (Major) and β-Si (Minor) Addition of Hydrogen to the Vinyl Silanes



to less than absolute regioselectivity of the hydrosilation reaction by which it was prepared (Scheme IV). Therefore, potential seven-membered-ring cycloparaffinsiloxane formation, which could occur in the networks, was also tested with this model. Though the degree of polymerization of **2** was only 10, significant amounts of the cyclic monomer and dimer were observed in the absence of dimethylsiloxy units with an equilibrium cyclic monomer concentration that was similar in magnitude to that for octamethylcyclotetrasiloxane in equilibrium with poly(dimethylsiloxane). However, as the amount of dimethylsiloxy units included in the composition increased, the cyclic monomer concentration decreased (Table II). The cyclic containing one unit from **2** and one or more dimethylsiloxy units increased until the ratio of dimethylsiloxy units to paraffinsiloxy units reached 8. As the proportion of dimethylsiloxy units increased further, the concentration of all of these cycloparaffinsiloxanes decreased until the concentration of all of these cyclics fell below detectable limits for the gas chromatographic conditions employed. This occurred at a dimethylsiloxy to paraffinsiloxy ratio of 64. The cyclic dimer decreased significantly more rapidly, and the cyclics composed of two paraffinsiloxy units and one or more dimethylsiloxy units were not observable at dimethylsiloxy to paraffinsiloxy ratios of 8 or greater.

Table II. Cycloparaffinsiloxane Concentrations for Various Copolymer Compositions

$[D]/[J^M]^a$	$[J^M{}_1]^b$	$[J^M{}_2]^c$	$\Sigma[D_xJ^M{}_y]^d$	$\Sigma[D_x]^e$
0	23.6	5.9	0.0	0.0
1	10.4	0.7	0.6	2.8
4	3.3	0.2	0.2	5.9
8	1.1	$<0.1^f$	$<0.1^f$	14.0
16	0.5	$<0.1^f$	$<0.1^f$	19.4
64	$<0.1^f$	$<0.1^f$	$<0.1^f$	26.1

[a] $[J^M]$ is the concentration of repeating units of the junction model from poly-**2**. [b] Cyclic monomer concentrations in moles/L × 100. [c] Cyclic dimer concentration in moles/L × 100. [d] Sum of the concentrations in moles/L × 100 where $x = 1, 2$ and $y = 1, 2$. [e] Sum of the concentrations in moles/L × 100 where $x = 1$–10. [f] Undetectable under the gas chromatographic conditions with all concentrations relative to the internal standard nonane.

This decrease in the concentration of the cycloparaffinsiloxanes was, as would be, anticipated qualitatively. The fraction of cyclics in a system decreases as the concentration increases.[31] When the ratio of dimethylsiloxy to paraffinsiloxy units in the mixture is high, the Si–O concentration is approximately five times that of the homopolymer from **2**. This result is consistent with what was previously observed for the reaction of oligocyclosiloxanes with an excess of hexamethyldisiloxane.[30] In that experiment, only fragments with retention times consistent with octamethyltrisiloxane and fully trimethylsilyl end-capped junctions were observed by a gas chromatographic analysis. No peaks were observed with the appropriate retention times to indicate the formation of cycloparaffinsiloxane, even though one might anticipate that the junctions of high functionality might favor cyclization relative to that of the difunctional model, the homopolymer of **2**, due to local concentration effects because of multiple Si–O units per molecule and since the concentration of Si–O bonds in hexamethyldisiloxane is much lower than it is in octamethylcyclotetrasiloxane. Thus, it appears reasonable to neglect cycloparaffinsiloxane formation in networks where the ratio of dimethylsiloxy units to junction exceeds 100 since the quantities of this type of defects should be very small relative to those of cyclodimethylsiloxanes.

Cyclosiloxane Composition and Sol Analysis. Though it is reasonable to neglect chain ends from acidolysis and cycloparaffinsiloxanes, cyclosiloxanes must be considered as they will account for more than 10% of the repeating units in the system at equilibrium, which includes most of the sol. The junctions were designed to act as dimethylsiloxy units which have been cross-linked for even-functionality junctions **4**, **6**, and **8**, or, additionally, dimethylsiloxy units which have been cross-linked with a single end link for odd functionalities **3**, **5**, and **7**. All of the dimethylsiloxy units on junctions are potential members of cyclosiloxanes. As the ratios of dimethylsiloxy units D to dimethylsiloxy units on junctions D^J used in this study were very large, the total concentration of cyclics should be that of cyclodimethylsiloxanes in equilibrium with high molecular weight poly(dimethylsiloxane). After experimentally determining the

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(30) Chang, P.-S.; Hughes, T. S.; Zhang, Y. C.; Webster, G. R.; Poczynok, D.; Buese, M. A. *J. Polym. Sci. Polym. Chem.* **1993**, *31*, 893.

(31) The cyclization which occurs during a polymerization of polyfunctional monomers always leads to error in predicting a gel point. The gel point as predicted by a Flory–Stockmayer treatment has been found to be correct when extrapolated to infinite concentration of the reactive functionality. Stockmayer, W. H. In *Advancing Fronts in Chemistry*; Twiss, S. B., Ed.; Van Nostrand Reinhold: New York, 1945; Chapter 6.

(32) (a) Sharaf, M. A. *Macromol. Rep.* **1993**, *A30*, 83. (b) Sharaf, M. A. *Int. J. Polym. Mater.* **1992**, *18*, 237. (c) Sharaf, M. A.; Mark, J. E. *Macromol. Rep.* **1991**, *1*, 67.

Table III. Partial Sol Analysis of Selected Networks

compd no.	mass of D_4 (g)	mass of oligocyc (g)	$[D_4]_{network}/[D_4]_{linear}$		$[D_5]_{network}/[D_5]_{linear}$	
			calcd	obsvd	calcd	obsvd
4	5.0000	0.4363	0.87	0.88	0.85	0.85
4	5.0000	0.2125	0.95	0.94	0.93	0.92
8	5.0000	0.7904	0.87	0.88	0.85	0.85
8	5.0000	0.3744	0.93	0.94	0.94	0.92

concentration of octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane in equilibrium with high molecular weight polymer, the values for the equilibrium cyclization constants K_x determined by Semlyen and Wright[18a] were chosen over the other reported values for these calculations. To simplify the calculations, only the cyclic 4-mers–21-mers were considered in this model since they account for more than 95 mol % of the cyclics for all sets of reported equilibrium cyclization constants. Furthermore, the difference in the sum of only K_4 through K_{10} for the different sets of reported cyclic equilibrium constants exceeded the concentration of the cyclics ignored by the limitation of ring sizes considered for the 4-mers–21-mers.

The concentrations of cyclics containing randomly placed D and D^J units were determined by the equation:

$$[D_xD^J{}_y] = K_{x+y}p^{x+y}\frac{(x+y)!}{x!y!}\left(\frac{[D]}{[D]+[D^J]}\right)^x\left(\frac{[D^J]}{[D]+[D^J]}\right)^y$$

where p is the probability of finding a difunctional unit rather than a monofunctional unit as one proceeds along a linear chain, which in a linear polymerization is related to the linear polymer's degree of polymerization[22] by the common expression

$$X_n = \frac{1}{1-p}$$

As seen in the equation for the cyclic concentrations, the probabilities of the placement of D and D^J units in a cyclic are their mole fractions, which are equal to their probabilities of being found along a chain of the network. The proportion of cyclics which incorporate junction units decreases as the mole fraction of D^J units decreases. The proportion of D^J units in cyclics which are members of cyclics with only one D^J unit increases as the mole fraction of D^J units decreases. When the ratio of D to D^J is greater than 100 as in the networks prepared for this study, the proportion of D^J units which are incorporated into cyclics remains effectively constant. At low D to D^J ratios, the total Si–O concentration decreases, which raises the weight fraction of cyclics in the mixture and, hence, the proportion of D^J units in cyclics. On the other hand, when an odd-functionality oligocyclic, **3**, **5**, or **7**, is used, the probability of encountering a monofunctional-like unit on a junction increases which lowers the value of p and the weight fraction of cyclics. For this reason, all networks were prepared with a high D to D^J ratio such that p could be assigned the value of 1 for all calculations. The minimum p for the network compositions that was used exceeded 0.997.

To test that this treatment correctly calculated the placement of D and D^J units in the equilibrium networks, four rubbers were prepared using oligocyclosiloxanes **4** or **8** and the extracted sols were analyzed by gas chromatography (Table III). The even-functionality oligocyclosiloxanes were chosen because a relatively highly cross-linked network is required to cause a large perturbation of the equilibrium concentrations of the smallest cyclosiloxanes D_4 and D_5. The use of an odd-functionality oligocyclosiloxane would have necessitated the consideration of the value of p to account for the effect of the trialkylsiloxy units on the junctions. The largest and smallest even-functionality junctions were chosen, since if cycloparaffinsiloxane formation was significant, the decrease in the concentrations of D_4 and D_5 would not be as great as anticipated and the deviation should be greater using **8** than it would be using **4**. The observed fraction of D_4 and D_5 relative to that of a D^J free polymer was very close to that predicted for each ratio of D and D^J units and for both oligocyclosiloxanes as shown in Table III. Hence, this equation closely predicted the populations of the various cyclics in the system. Since the observed cyclosiloxane fractions were not systematically higher than predicted, cycloparaffinsiloxane formation, which removes D^J units, was not indicated.

The equilibrium structure was achieved in less than a day with these compositions. To assure the establishment of equilibrium with the more lightly cross-linked networks prepared in this study, termination of the active center was carried out more than a week after gelation.

Junction Structure and Functionality. To address the effect of cyclization on junction functionality, the cyclosiloxanes were grouped as four different types. The first type were the cyclosiloxanes which contained no junction units. They constituted the majority of the sol in equilibrium with the network. The second type of cyclosiloxanes, ^1C, were those which contained a single D^J unit. These cyclics were defects to the junctions which decreased the functionality of the junction by two. For example, a tetrafunctional junction site, which consists of two D^J units, becomes a difunctional unit if one of the D^J units is a member of this type of ring. The third type of cyclosiloxanes, ^2C, were those which contained two junction units. These structures coupled two junctions. These structures may affect the number and functionality of the junctions in two different ways. They will either decrease the functionality of each junction connected to the cyclic by one or convert two junctions which without cyclic groups have a functionality of f into one junction with a maximum possible functionality of $2f-4$. The proper structural assignment depends upon whether the cyclosiloxane unit should be considered as an elastic or inelastic linkage in the network. Some studies have indicated that very small chains were probably misassigned as inelastic linkages.[32] Nevertheless, the size of the ring and the position of the two substituents should affect which assignment is correct. The treatment used in this paper is to assign the cyclic as an elastic chain and to reduce the functionality of each junction by one. With oligocyclosiloxane **3** as the source of junctions, the assignment of the pair of junctions becomes either one or two difunctional units. Because the concentration of D units is so much greater than the concentration of junctions, the difference in the concentration of difunctional units in the network is essentially the same by either treatment. The potential error from choosing the wrong treatment is also small, as the concentration of such cyclics is very low when the ratio of D to D^J is large, as was the case for this study. The fourth type of cyclics, ^3C, were those which contained three or more D^J units. Again, the links between junctions were considered to be elastic; hence, their occurrence did not decrease the functionalities of the junctions included in the cyclics. Conversely, the joining of y junctions of functionality f would result in one junction of functionality $y(f-2)$ if the units of the ring between the junctions were inelastic elements. The concentration of cyclics which contain three or more junctions is extremely small when the D to D^J ratio is very large; hence, the errors resulting from junction misassignment should be extremely small.

Each junction J consists of cross-linking core connected to D^J units which creates a branch, B, on the primary chain of the network, or the D^J units are part of a cyclic containing no other junctions, ^1C, one other junction, ^2C, or two or more other junctions, ^3C. The four different units should be attached randomly to the junction cores, and the concentrations of the different functionalized junctions were calculated by the equation:

$$[J(B)_w(^1C)_x(^2C)_y(^3C)_z] = [J](B)^w(^1C)^x(^2C)^y(^3C)^z\frac{(w+x+y+z)!}{w!x!y!z!}$$

where

Table IV. Junction Composition for Various Proportions of D and D^J Units

compd no.	[D]/[D^J]	percent of junctions with functionality of 1	2	3	4	5	6	7	8
3	99	12.1	0.582	87.3					
3	399	12.4	0.154	87.4					
4	99	0.139	20.9	1.02	76.5				
4	399	0.038	21.7	0.268	76.5				
5	99	1.44	0.141	21.0	1.03	76.4			
5	399	1.54	0.038	21.7	0.269	76.5			
6	99	0.025	3.77	0.367	27.5	1.34	66.8		
6	399	0.007	4.03	0.100	28.4	0.352	66.9		
7	99	0.173	0.026	3.79	0.371	27.6	1.35	66.7	
7	399	0.191	0.007	4.04	0.100	28.5	0.352	66.9	
8	99	0.004	0.600	0.088	6.58	0.643	32.0	1.57	58.5
8	399	0.001	0.666	0.025	7.05	0.174	33.2	0.410	58.5

$$w + x + y + z = \frac{f}{2}\ (\text{for } f = \text{even}),\ w + x + y + z = \frac{f-1}{2}\ (\text{for } f = \text{odd})$$

and the probabilities that a D^J is part of a cyclic or a chain are

$$({}^1\mathrm{C}) = \frac{\sum_{x=3}^{20}[\mathrm{D}_x\mathrm{D}^J]}{[\mathrm{D}^J]}$$

$$({}^2\mathrm{C}) = \frac{\sum_{x=2}^{19}2[\mathrm{D}_x\mathrm{D}^J{}_2]}{[\mathrm{D}^J]}$$

$$({}^3\mathrm{C}) = \frac{\sum_{n=4}^{21}\sum_{y=3}^{n}y[\mathrm{D}_{n-y}\mathrm{D}^J{}_y]}{[\mathrm{D}^J]}$$

$$(\mathrm{B}) = 1 - {}^1\mathrm{C} - {}^2\mathrm{C} - {}^3\mathrm{C}$$

The functionalities of the junctions were calculated by the equation:

$$f_{[\mathrm{J(B)}_w({}^1\mathrm{C})_x({}^2\mathrm{C})_y({}^3\mathrm{C})_z]} = f - 2x - y$$

As seen in Table IV, the fraction of perfect junctions, those which contain no ^{1}C and ^{2}C groups, decreases with the maximum functionality of the junction. As the ratio of D to D^J increases, the proportion of junctions which have functionalities $f - 2x$, where x is an integer, increases since the proportion of the cyclics that are ^{1}C rather than ^{2}C and ^{3}C increases. More than 90% of the junctions are f or $f - 2$ at high D to D^J ratios. Those networks made from even-functionality oligocyclosiloxanes require a ^{2}C and one or more ^{1}C cyclics to become monofunctional (Figure 7) and are therefore very low in concentration. The networks prepared from odd-functionality oligocyclosiloxanes require one or more ^{1}C cyclics to become monofunctional (Figure 7); hence, they are more numerous. Because multiple ^{1}C cyclics are necessary for networks from **5** and **7**, the concentration of monofunctional units is high only for networks prepared from **3** (Table IV).

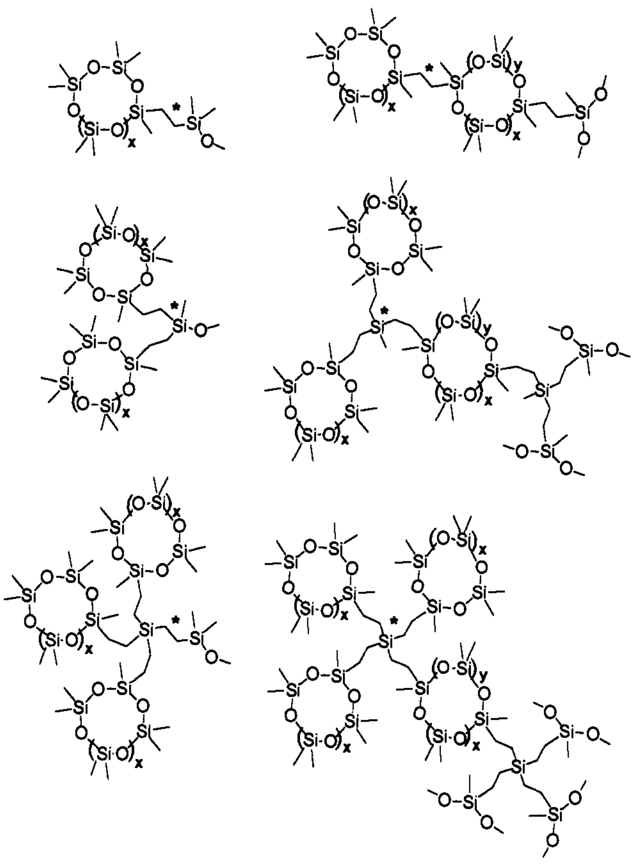

Figure 7. Monofunctional junctions (marked with an asterisk) which form in networks from **3**, **5**, and **7** (left column, top to bottom, respectively) and from **4**, **6**, and **8** (right column, top to bottom, respectively).

Network Structure and Swelling Studies. To test that this statistical treatment could define the detailed microstructure of the networks, swelling was examined for networks with different functionalities of junctions but with virtually identical calculated average functionalities. Mechanical testing was not chosen for this initial study because macroscopic defects and errors in measuring the sample dimensions affect the observed modulus. In theory, the swelling of a rubber occurs to an extent where the increase in entropy of the network–solvent system upon dilution of the network balances the decrease in entropy of the polymer chain by isotropic dilation.[33] Networks were prepared where the average functionality of the network was kept low and essentially constant (Table V). The average functionalities of the networks were calculated by the equation:

$$\mathrm{AF} = \frac{2[\mathrm{D_B}] + \sum_{f_{[\mathrm{J}]}\geq 1} f_{[\mathrm{J(B)}_w({}^1\mathrm{C})_x({}^2\mathrm{C})_y({}^3\mathrm{C})_z]}[\mathrm{J(B)}_w({}^1\mathrm{C})_x({}^2\mathrm{C})_y({}^3\mathrm{C})_z]}{[\mathrm{D_B}] + \sum_{f_{[\mathrm{J}]}\geq 1}[\mathrm{J(B)}_w({}^1\mathrm{C})_x({}^2\mathrm{C})_y({}^3\mathrm{C})_2]}$$

where D$_\mathrm{B}$ is dimethylsiloxy units in the chains between junctions whose concentration is given by the expression

$$[\mathrm{D_B}] = [\mathrm{D}] - \sum_{x=4}^{21}x[\mathrm{D}_x] - \sum_{x=3}^{20}x[\mathrm{D}_x\mathrm{D}^J] - \sum_{x=2}^{19}(3x/4)[\mathrm{D}_x\mathrm{D}^J{}_2] \approx [\mathrm{D}] - \sum_{x=4}^{21}\sum_{y=0}^{x-y}(x-y)[\mathrm{D}_{x-y}\mathrm{D}^J{}_y]$$

As indicated in this expression, the D units on cyclics in the sol and ^{1}C cyclics and approximately one-half of the D units on ^{2}C cyclics are not elements of the network considered in its topology. Since the concentration of ^{2}C and ^{3}C cyclics is so small, [D$_\mathrm{B}$] is essentially equal to the concentration of D units which are not incorporated into cyclosiloxanes.

The average functionality of the network was chosen because of its relationship to the cycle rank[3] of the network ξ if the network is perfect and lightly cross-linked. For a perfect network, the

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(33) (a) Flory, P. J.; Rehner, J., Jr. *J. Chem. Phys.* **1943**, *11*, 521. (b) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51. (c) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.

Table V. Network Formulations

sample[a]	(AF − 2) × 100[b]	(AF′ − 2) × 100[c]	D_4[d]	oligocyc[d]	[D][e]	[J] × 100[e]
3a	0.98	1.15	10.0000	0.0583	13.1	1.51
4a	0.99	1.13	10.0000	0.0281	13.1	0.742
5a	0.99	1.04	10.0000	0.0315	13.1	0.457
6a	0.99	1.07	10.0000	0.0351	13.1	0.351
7a	1.00	1.02	10.0000	0.0291	13.1	0.269
8a	1.00	1.04	10.0000	0.0298	13.2	0.229
3b	1.97	2.29	10.0000	0.1172	13.1	3.01
4b	1.97	2.25	10.0000	0.0563	13.1	1.48
5b	1.99	2.09	10.0000	0.0632	13.1	0.914
6b	2.05	2.21	10.0000	0.0728	13.1	0.726
7b	2.00	2.05	10.0000	0.0584	13.1	0.539
8b	1.99	2.02	10.0000	0.0597	13.1	0.457
3c	4.92	5.73	10.0000	0.2970	13.0	7.49
4c	4.94	5.63	10.0000	0.1415	13.1	3.69
5c	4.98	5.23	10.0000	0.1592	13.1	2.28
6c	4.97	5.33	10.0000	0.1771	13.1	1.75
7c	5.06	5.21	10.0000	0.1492	13.1	1.36
8c	4.98	5.22	10.0000	0.1502	13.1	1.14
3c′	4.30	5.00	10.0000	0.2587	13.1	6.55
4c′	4.39	5.00	10.0000	0.1256	13.1	3.28
5c′	4.77	5.00	10.0000	0.1524	13.1	2.19
6c′	4.65	5.00	10.0000	0.1659	13.1	1.64
7c′	4.90	5.04	10.0000	0.1444	13.1	1.32
8c′	4.77	5.00	10.0000	0.1438	13.1	1.09

[a] Number refers to the compound used as the source of junctions. [b] Average functionality calculated assuming cyclization as in the model. [c] Average functionality assuming no cyclization. [d] Mass in grams. [e] Concentration in moles/L.

average functionality is given by the expression:

$$\mathrm{AF} = \frac{2\mathrm{D} + \varphi\mu}{\mathrm{D} + \mu}$$

where φ is the average functionality of the junction, μ is the number of junctions in the reference volume, and D is the number of difunctional units in the reference volume. The cycle rank is defined as:

$$\xi = \frac{\varphi\mu}{2} - \mu$$

When the average functionality is low, AF $\approx$ 2 and these two equations can be combined to yield

$$\mathrm{AF} - 2 = \frac{(\varphi - \mathrm{AF})\mu}{\mathrm{D}} \approx \frac{(\varphi - 2)\mu}{\mathrm{D}} = \frac{2\xi}{\mathrm{D}}$$

This may be a useful relationship in assessing whether equilibrium has been established in other networks prepared via a living percolation mechanism where analysis of the sol is not a viable option. Only at equilibrium should the cycle rank be related to the average functionality of the reagents using this expression.

In this study, network formulations were designed assuming that the Flory–Huggins polymer–solvent interaction parameter χ[34] would effectively be a constant for all networks since the junctions were a small fraction of the chain-link elements. Therefore, if the average functionality and ξ were the same for any two networks, they should display nearly the same volume fraction of network in the equilibrium swollen state ν_{2m}. The fraction of D units incorporated between junctions in our compositions resulted in a 2/D value of 0.173. This factor is the observed difference between the calculated average functionality minus two of the network and ξ for all networks made from oligocyclics **4**–**8** where, as seen in Table VI, the number of monofunctional defects should be very small. This was not the case with oligocyclic **3**, where the number of monofunctional junctions is very high. Table VI shows that the observed volume fraction of network was essentially equal for networks of the same average functionality except for those prepared from **3**.

The calculated sizes of the primary chain and the sizes of the chain between junctions are also given in Table VI. As indicated in the introduction, typically, it is very difficult to reliably prepare model networks which have an average molecular weight between cross-links in excess of 20 000. Because the percolation mechanism is a chain-growth process, stoichiometry is relatively easily maintained fron one sample to another regardless of the size of the chain between junctions. The average size of the chains between junctions in this study was always greater than 8000 and exceeded 100 000 in two cases. Within a series of networks with the same average functionality, the size of the chain between junctions increased by over 60%. The size of the primary chain was more than 360 times that of the chain between junctions except for those networks prepared from **3**, where the primary chain was approximately 25 times the size of the chain between junctions. This ratio decreases slightly as the average functionality decreases for the networks prepared from **3**, **5**, and **7** but increases significantly as the average functionality decreases for the networks prepared from **4**, **6**, and **8**. It may be more appropriate to view the monofunctional junctions in the networks from **4**, **6**, and **8** as large pendant groups on defective junctions rather than as true chain ends. Doing so would further increase the calculated size of the primary chains in these networks. Termination by side reactions with impurities in quantities greater than the parts per thousand level would be required to reduce the actual size of the primary chain such that a significant deviation in the true cycle rank from that calculated would occur for the networks prepared from **4**–**8**.

It is interesting to point out that nearly all model networks have been prepared by end linking polymers to reagents which are either tri- or tetrafunctional. In those systems, it has been assumed that the molecular weight and distribution of weights between junctions were exactly the same as those of the telechelic polymers used. It was also been assumed that the reactive groups resided on all chain ends, that the stoichiometry between the large molecular weight chain and the polyfunctional reagent was perfect, and that the reaction proceeded in an exclusive and exhaustive manner such that the functionality of all junctions was that of the polyfunctional reagent. Assuming that the junction functionalities were always their maximum for an isolated junction and that all D units were incorporated between junctions, compositions were formulated which resulted in the networks with the uncorrected average functionality of 2.005 in Table V and Figure 8. The observed difference in swelling from that of networks whose structure was assigned by this model was greater as the junction functionality decreased. The presence of junctions with functionalities of one or two caused the greatest deviation in the observed swelling (networks from **3** and **4** in Figure 8). Where the concentration of junctions with functionalities less than three was very small, as in the case of networks made from **7** and **8**, the deviation was small. The effect of a monofunctional is much more pronounced than that of difunctionals. This is reflected in the significant difference observed for the networks made from **5**, while those made from **6** showed little difference even though the concentration of difunctional junctions from **6** was nearly three times the concentration of monofunctional units from **5**, as implied in Table IV. This suggests that in previous model studies, when the primary junction functionality was three or four, deviations from stoichiometry, selectivity, or conversion of only 1% could lead to significant errors in the assignments of network structure regardless of the presence of entanglements, loops, or other topology defects.

This treatment does not take into consideration that the sol would contain any junctions that have a calculated functionality greater than zero. When the fraction of junctions which are monofunctional is approximately 0.01 or less, the concentration of junctions in the sol will be negligible. Only in the case of the networks prepared from **3** is the fraction of junctions in the sol of consequence. However, the loss of monofunctional capped linear and branched polymers in the sol increases the average

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(34) (a) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660. (b) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.

Table VI. Network Topology and Equilibrium Swelling Results

sample	ξ^a	μ^a	φ	$\nu_{2m} \times 100^b$	$M_c{}^c$	$M_n{}^d$	$\chi_p{}^e$	$\chi_a{}^f$
3a	6.27	12.5	3.00	9.98 ± 0.01	4.11×10^4	9.08×10^6	0.498	0.536
4a	5.68	5.68	4.00	13.70 ± 0.01	6.57×10^4	1.32×10^9	0.531	0.551
5a	5.72	4.48	4.55	13.73 ± 0.01	8.29×10^4	2.39×10^7	0.531	0.551
6a	5.71	3.36	5.40	13.72 ± 0.01	9.25×10^4	2.09×10^{10}	0.531	0.551
7a	5.72	2.69	6.26	13.65 ± 0.01	1.01×10^5	3.24×10^8	0.530	0.551
8a	5.72	2.27	7.03	13.65 ± 0.01	1.06×10^5	2.21×10^{11}	0.530	0.551
3b	12.5	25.1	3.00	10.25 ± 0.01	2.10×10^4	4.56×10^5	0.464	0.537
4b	11.4	11.4	4.00	14.92 ± 0.01	3.28×10^4	3.36×10^8	0.521	0.556
5b	11.5	8.97	4.56	14.98 ± 0.01	4.14×10^7	1.20×10^7	0.521	0.556
6b	11.8	6.95	5.40	14.95 ± 0.01	4.47×10^4	4.96×10^9	0.520	0.556
7b	11.5	5.39	6.26	14.97 ± 0.01	5.05×10^4	1.63×10^8	0.521	0.556
8b	11.4	4.54	7.04	14.93 ± 0.01	5.32×10^4	5.62×10^{10}	0.521	0.556
3c	31.2	62.4	3.00	19.88 ± 0.01	8.18×10^3	1.85×10^5	0.518	0.577
4c	28.4	28.5	3.99	21.74 ± 0.03	1.31×10^4	5.62×10^7	0.540	0.586
5c	28.6	22.4	4.56	21.64 ± 0.03	1.65×10^4	4.90×10^6	0.538	0.586
6c	28.5	16.7	5.40	21.49 ± 0.01	1.85×10^4	8.84×10^8	0.537	0.585
7c	29.0	13.6	6.26	21.39 ± 0.04	1.99×10^4	6.59×10^7	0.535	0.585
8c	28.5	11.3	7.04	21.31 ± 0.03	2.13×10^4	9.41×10^9	0.536	0.585
3c′	27.3	54.6	3.00	18.17 ± 0.01	9.37×10^3	2.11×10^5	0.509	0.569
4c′	25.2	25.3	3.99	20.04 ± 0.04	1.48×10^4	7.06×10^7	0.531	0.578
5c′	27.4	21.4	4.56	20.74 ± 0.01	1.73×10^4	5.11×10^6	0.533	0.582
6c′	26.7	15.7	5.40	21.31 ± 0.03	1.97×10^4	1.00×10^9	0.539	0.584
7c′	28.1	13.2	6.26	21.22 ± 0.03	2.05×10^4	6.80×10^7	0.536	0.584
8c′	27.3	10.8	7.04	21.17 ± 0.03	2.22×10^4	1.02×10^{10}	0.536	0.584

[a] In mmoles/L. [b] Average of three samples at 25 °C. [c] Calculated average molecular weight of chains between junctions. [d] Calculated average molecular weight of primary chains. [e] Calculated from: $\ln(1 - \nu_{2m}) + \chi(\nu_{2m})^2 + \nu_{2m} = \xi V_1(\nu_{2m})^{1/3}$ where V_1 is the molar volume of hexane. [f] Calculated from the equation: $\ln(1 - \nu_{2m}) + \chi(\nu_{2m})^2 + \nu_{2m} = \xi V_1(\nu_{2m})^{1/3}\{1 + (\mu/\xi)[1 - (\nu_{2m})^{2/3}]\}$.

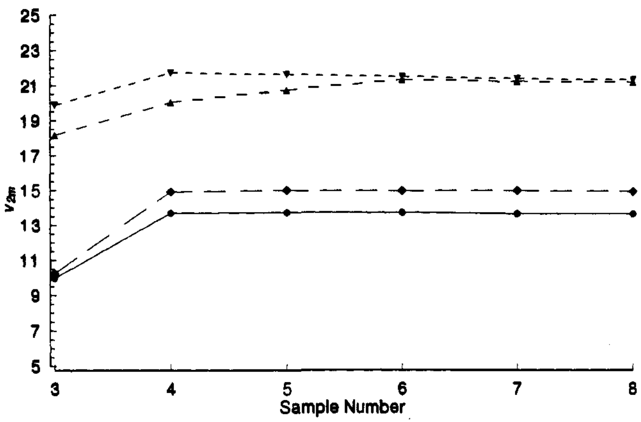

Figure 8. Volume fraction of the network at equilibrium for networks of equivalent average functionality networks when corrected by the model series **3a**–**8a** (•), **3b**–**8b** (◆), and **3c**–**8c** (▼), and uncorrected by the model, series **3c′**–**8c′** (▲).

functionality of the network, since more monofunctional than polyfunctional junctions are necessarily lost. The networks prepared from **3** all swelled to a much greater extent than others designed with the same average functionality. Junction functionality was calculated only on the basis of whether a cyclic or a chain was connected to a Si–O group of that junction, which shall be referred to as the first level of connectivity. Calculations of junction functionality at this level of connectivity result in an overestimation of the number of active chains because they do not take into consideration the amplifying effect of the monofunctional capped dangling chains due to the connectivity of one junction to another junction via a chain which would constitute the second level of connectivity. This second level of connectivity was previously considered by Case[35] and Scanlan[36] for tetrafunctional junctions prepared by randomly cross-linking primary chains. This effect on the number of active chains is more pronounced when the average functionality of the junctions in the network is small. A junction must be reduced in functionality to less than three by the coincidence of its connectivity to monofunctional junctions to incorrectly assign the number of active chains by considering only the first level of connectivity.

As seen in Table VI, the reduction in the number of active chains by the few monofunctional junctions does not appear to be amplified by the second level of connectivity of junctions for networks prepared from **4**–**8**, as they displayed virtually identical swelling. Even in the case of the networks prepared from **5**, where monofunctional junctions slightly exceed 1% of all junctions, no systematic deviation in the degree of swelling was observed relative to that of the other members of the series. In the networks prepared from **5**, the junctions of functionality five provided over 80% of the sites to which a monofunctional can be attached. Attachment of a monofunctional end-capped chain to a junction forms only one inactive chain when the junction's functionality is reduced to only four or three and those inactive chains are accounted for at the first level of connectivity.

The values of χ calculated from the observed ν_{2m} for all networks made with oligocyclics **4**–**8** were all within 2.1% of the average value of 0.531 when the common expression relating swelling to the phantom network was used and within 3.2% of the average value of 0.569 when the common expression relating swelling to the affine network was used.[3] No calculations were made using equations which include terms for interpenetration and inhomogeneities in network topology.[3] With very lightly cross-linked networks, those with average functionalities of 2.001 and 2.002, the value of χ from calculations assuming phantom networks decreased as ν_{2m} increased, as has been observed with uncross-linked linear high molecular weight poly(dimethylsiloxane) in cyclohexane.[37] However, when χ was calculated assuming affine networks and assuming phantom networks when the average functionality of the network was higher, where the molecular weight between junctions was in the range of other model networks, its value increased with the functionality of the network, as has been observed[38] and was predicted from theoretical considerations.[39] This laboratory intends to address this point in greater detail only after completion of more extensive and rigorous swelling studies.

In conclusion, a novel living percolation method for network

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preparation has been demonstrated which permits the assignment of the final network structure from a simple statistical treatment of the ring–chain equilibrium involved in the preparation of the network. An analysis of the equilibrium sol indicated that the distribution of rings was as calculated. Networks where the majority of junctions had functionalities of three through eight were compared. Since defective junctions were the only significant source of monofunctional units in the networks, those with primarily tetrafunctionalities or higher functionalities behaved as nearly perfect networks. The percolation mechanism appears to be a superior method for preparing model networks since the structure of the network at equilibrium depends only on the initial composition and permits the consistent preparation of very lightly cross-linked networks.

Experimental Section

General Procedure. Oligocyclodimethylsiloxanes were prepared and isolated as previously reported.[30] Octamethylcyclotetrasiloxane was purchased from Hüls and used after distillation and verification of purity by gas chromatographic analysis. Nonane (99.9%) and trifluoromethanesulfonic acid were purchased from Aldrich and used as received. Magnesium oxide (light powder) and *n*-hexane (HPLC grade) were used as received from Fisher. Hexamethyldisiloxane, pentamethyldisiloxane, trimethylsilane, and a divinyldisiloxane-complexed platinum hydrosilation catalyst were used as received from Hüls.

Gas chromatographic analysis was performed on a Hewlett-Packard 5890A chromatograph equipped with a thermal conductivity detector. A 6-ft. × $^1/_8$-in. column packed with 5% OV-101 was used with a temperature gradient from 60 to 250 °C at 10 °C/min after 2 min at 60 °C and then held at maximum temperature for 2 min. Proton NMR spectra were recorded using a GE NQ 300 spectrometer. Infrared spectra were recorded on a Mattson Series 4020 FTIR spectrometer.

Viscosity Experiments. Trimethylsilyl end-capped poly(dimethylsiloxane) was prepared by the addition of 5 μL of trifluoromethanesulfonic acid and a mixture of 37.79 g of octamethylcyclotetrasiloxane and 0.138 g of hexamethyldisiloxane where the ratio of dimethylsiloxy to trimethylsiloxy units was 300. After equilibrium was established as indicated by a gas chromatographic analysis of the volatile oligomers in MgO-quenched aliquots, 0.5 g of MgO was added to the equilibrated mixture to quench the reaction. The sample was centrifuged at 3700 rpm for 2 h using a Marathon 6K centrifuge. A 6.82-mL sample of the MgO-free fluid was analyzed using a calibrated Canon-Fiske viscometer (Kinematic 400) at 40, 70, and 100 °C under a nitrogen atmosphere. Trifluoromethanesulfonic acid (2 μL) was introduced, and the viscosity of the fluid was measured. The reaction was again quenched with MgO, the living fluid was centrifuged, and the viscosity of the MgO-free fluid was determined.

Synthesis of Bis[2-((trimethylsiloxy)dimethylsilyl)ethyl]vinylmethylsilane (1). The synthesis of **1** (Scheme IV) was carried out by hydrosilation of 5.0 g of methyltrivinylsilane with 11.3 g of pentamethyldisiloxane using 5 μL of hydrosilation catalyst at 70 °C. A yield of 24% was isolated by distillation at 85–87 °C under vacuum (1 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.01 (s, 3 H), 0.02 (s, 12 H), 0.08 (s, 18 H), 0.41 (m, 4 H), 0.50 (m, 4 H), 5.68 (AMX, J_{AM} = 19.8 Hz, J_{AX} = 4.5 Hz, 1 H), 6.00 (AMX, J_{MX} = 14.7 Hz, J_{AX} = 4.5 Hz, 1 H), 6.14 (AMX, J_{AM} = 19.8 Hz, J_{MX} = 14.7 Hz, 1 H). Anal. Calcd for $C_{17}H_{44}Si_5O_2$: C, 48.51; H, 10.54; Si, 33.36; O, 7.60. Found: C, 48.14; H, 10.84.

Synthesis of 2. The hydrosilation of 2 g of **1** with an excess (1.73 g) of trimethylsilane (Scheme IV) in 10 mL of toluene using 2 μL of the hydrosilation catalyst in a thick-walled sealed tube resulted in the formation of **2** which was isolated in 52% yield by distillation at 108–114 °C under vacuum (1 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ –0.07 (s, 3 H), –0.01 (s, 9 H), 0.06 (s, 12 H), 0.08 (s, 18 H), 0.40 (m, 12 H). IR (neat liquid on NaCl): cm^{-1} 2957 (s), 2879 (s), 2791 (w), 1934 (w), 1579 (m), 1406 (m), 1252 (s), 1131 (s), 1051 (s), 812 (s), 687 (s), 624 (m), 491 (s). Anal. Calcd for $C_{20}H_{54}Si_6O_2$: C, 48.51; H, 10.99; Si, 34.03; O, 6.46. Found: C, 48.39; H, 11.22.

Polymerization of 2. The condensation polymerization of **2** (Scheme II) was carried out by distilling hexamethyldisiloxane from a mixture of 1 g of **2** and 1 μL of trifluoromethanesulfonic acid in 20 mL of toluene at 90 °C. A viscous, colorless, liquid polymer was obtained. NMR spectra indicated that a degree of polymerization of 9.6 was achieved from the ratio of the integrated signals of the methyl groups to the methylene groups. A gas chromatographic and ^{1}H NMR analysis indicated the formation of a cyclic monomer and dimer from **2**. ^{1}H NMR (300 MHz, $CDCl_3$): δ –0.09 (s, 3 H), –0.06 (s, 9 H), 0.08 (s, 12 H), 0.10 (s, 3 H), 0.41 (m, 10 H), 0.60 (m, 1 H), 0.67 (m, 1 H).

Redistribution of Poly-2 with Octamethylcyclotetrasiloxane. Nonane (3.6×10^{-3} g) was introduced via a microliter syringe into 7.6×10^{-2} g of the homopolymer from **2** with 0:5 μL of trifluoromethanesulfonic acid, and aliquots of octamethylcyclotetrasiloxane were sequentially added to achieve the desired comonomer ratios upon redistribution (Scheme III). Gas chromatographic analyses were carried out after each addition of octamethylcyclotetrasiloxane until no change was observed in the oligomer composition. The concentrations of various cyclics were calculated from the relative area ratios of these cyclics to that of the internal standard (nonane), assuming a weight response for all components.

Sol Analysis. Networks were prepared using various compositions of octamethylcyclotetrasiloxane with polycyclosiloxanes **4** or **8** (Table III) such that the ratio of dimethylsiloxy to dimethylsiloxy-like units of the junctions was 30 or 60. A 0.400-g portion of the resulting networks was buried in MgO for a week and then swollen in 4 mL of toluene in the presence of 20 μL of nonane as an internal standard for 4 days. The toluene sol extracts were analyzed by gas chromatography. The concentrations of octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane extracted from the networks were calculated from the area ratios of cyclics to that of nonane. The relative response factors for octamethylcyclotetrasiloxane and nonane were determined by analysis of the mixture of 0.0100 g of nonane and 0.0100 g of octamethylcyclotetrasiloxane. The concentrations of these cyclics were compared with those formed by the homopolymerization of octamethylcyclotetrasiloxane upon addition of trifluoromethanesulfonic acid.

Network Preparation. The networks were prepared by the addition of trifluoromethanesulfonic acid to mixtures of octamethylcyclotetrasiloxane and an oligocyclodimethylsiloxane. The two siloxane reagents were mixed in proportions to give a desired ratio of difunctional to polyfunctional units which would result in a desired average functionality of the network as calculated from the statistical treatment developed. These compositions are given in Table V. The siloxane mixture was cured in a polyethylene vial by the addition of 2 μL of the acid, resulting in a concentration of 2.25×10^{-3} M. After 7 days, the cured networks were removed by cutting the vials and the networks were buried in MgO for an additional 7 days to quench the reaction of the acid catalyst.

Swelling Studies. Swelling experiments were carried out by placing a piece of the network which was cut from the "dead" rubber in hexane after washing the MgO from its surface under a stream of water. The swollen network was transferred into fresh hexane after 24 h. The swollen network was transferred into fresh hexane five times until the unabsorbed hexane displayed no cyclosiloxanes by gas chromatographic analysis. The swollen networks were then desolvated by heating to 60 °C in a vacuum oven at 15 mmHg for 2 days. Samples were cut from the network and placed in fresh hexane until the weight of the swollen network for lightly patted-dry samples was constant. The thermal history of all network samples was identical and maintained at 25 °C.

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