

Deformation Behavior of Poly(dimethyl siloxane) Networks. I. Applicability of Various Theories to Modulus Prediction

S. VENKATRAMAN*

Corporate Technology, Raychem Corporation, Menlo Park, California 94025

SYNOPSIS

The shear moduli of end-linked poly(dimethyl siloxane) networks were measured as a function of mol wt between chemical crosslinks (M_c) and the dilution-at-cure (C_x). The results were interpreted in terms of theories that take into account contributions from trapped entanglements. It was found that the network deformation follows the predictions of the theory of "phantom" networks, with an added contribution from trapped entanglements. At high mol wts of the precursor polymer, network imperfections play a role, as seen in the frequency dependence of the shear modulus. This results in deviation from predicted behavior. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

There have been a number of studies on the elastic behavior of networks; most of these have been summarized in two extensive review articles.^{1,2} Many of these studies have focussed on the applicability of various theories to the prediction of the magnitude of the modulus³⁻⁶ or of the degree of swelling.^{7,8} The theories examined can be broadly divided into two classes: those that recognize the contribution from permanent interchain constraints ("entanglements") and those that do not. In our work, we measured the elastic properties of end-linked poly(dimethyl siloxane) or PDMS networks, and analyzed the results in the light of these two types of theories. The shear moduli and the degree of swelling were measured as a function of two variables: the mol wt between chemical crosslinks (M_c) and the dilution-at-cure (C_x). We believe the range of these variables that we have covered is wider than has been reported in any one study. In Part I of this series is an examination of the dependence of the shear modulus on the above two variables; in a subsequent publication the swelling characteristics of the same networks will be reported.

THEORETICAL OVERVIEW

Flory and Rehner,⁹ in their derivation of network properties, assumed that the crosslink junctions were fixed in space, at least during the time scale of the deformation under consideration. For this type of network, also called an "affine" network, the changes in macroscopic dimensions were equal to the changes in molecular dimensions between junction points. For the shear moduli, the theory predicts:

$$G_{\text{aff}} = \nu RT \quad (1)$$

where ν is the number of network chains per unit volume.

The theory of James and Guth¹⁰ allows for junction fluctuations around an average position. For this type of network, also referred to as "phantom," the modulus is predicted to be:

$$G_{\text{ph}} = \beta RT \quad (2)$$

where β is the "cycle rank" of the network, or the number of chains that have to be cut in order to reduce the network to a collection of star molecules. For "perfect" networks, that is, networks with no dangling chains, β is related to the number of chains per unit volume, ν :

* Present address: Cygnus Therapeutic Systems, 400 Penobscot Drive, Redwood City, California 94063.

$$\beta = (\nu - \mu) = [\nu - (\nu/\phi)] \quad (3)$$

where μ is the number of junctions and ϕ is the functionality of a network junction.

Flory,¹¹ and Erman and Flory,¹² later combined the salient features of the phantom and affine models in the "constrained-phantom" network model. The fluctuations of the junctions now were allowed to be constrained by the presence of neighboring chains. The extent of this constraint was expressed by the parameter κ . At low κ , there was unrestricted junction mobility, or the phantom model was attained; at large κ , all fluctuation was suppressed and the affine limit was realized.

It was also postulated by the same authors that for small deformations, such as in low-strain modulus measurements, the constraints should exert their maximum influence (affine behavior). For large deformations, such as is involved in swelling, fluctuations should be less hindered (phantom behavior). Dossin and Graessley³ preferred to express this range of behavior in terms of an empirical parameter, h , which reflects the severity of constraints in junctions. Thus in their formalism,

$$\begin{aligned} G &= (\nu - h\mu)RT \quad 0 < h < 1 \\ h &= 0, G = G_{\text{aff}} \\ h &= 1, G = G_{ph} \end{aligned} \quad (4)$$

Bueche¹³ and Mullins¹⁴ attributed a greater role to entanglements than mere suppression of junction fluctuations. Later, Langley¹⁵ and Mancke et al.¹⁶ refined their concept of "trapped" entanglements and their contribution, as effective junction points, to elastic properties. In general, the entanglement contribution to the modulus can be written as

$$G_e = T_e G_e^0 \quad (5)$$

where T_e is the fraction of trapped entanglements that are permanently trapped, and G_e^0 is the plateau modulus of the corresponding linear polymer of the same backbone structure.

In the discussion here, we follow the formalism of Dossin and Graessley³ and write a general expression for the modulus

$$G = G_c + G_e = (\nu - h\mu)RT + T_e G_e^0 \quad (6a)$$

or,

$$G = A\nu RT + T_e G_e^0; \quad A = (1 - h\nu/\phi) \quad (6b)$$

where the subscript c refers to chemical crosslinks and the subscript e refers to entanglements. Equation (6) is applicable to so-called "perfect" networks with few dangling chains, and may be valid only for small deformations.

The fraction of trapped entanglements, T_e , may be treated as an adjustable parameter or calculated from the branching theory. If the Langley definition of a trapped entanglement¹⁵ is used, along with the Flory criterion for counting them,¹⁷ the following expression results:

$$T_e = [(1/p)(1.5 - (1/rp^2 - (3/4))^{0.5})]^4 \quad (7)$$

where p = extent of reaction and r = reactant stoichiometric ratio.

The extent of the reaction may be recast in terms of the measurable quantity, sol fraction (w_s), using the Miller-Macosko¹⁸ approximation

$$T_e = [1 - (w_s/w_b)^{0.5}]^4 \quad (8)$$

where the assumption is made that all incomplete reactions led to sol fraction and that there are no side reactions that lead to sol fraction. Equation (8) is applicable to a $A_4 + B_2$ system, that is, a tetrafunctional molecule reacting with an oligomeric difunctional B_2 . In the equation, w_b is the initial weight of the B_2 oligomer in the reaction mixture.

Dependence on Dilution-at-Cure

For the case of networks prepared with a diluent, the modulus expression [Eq. (6)] must be modified to

$$G = (A\nu RT)C_x + T_e G_e(C_x) \quad (9)$$

where C_x is the network volume fraction or the weight fraction of "gel." The function $G_e(C_x)$ is undefined, but may be expected to be a power law from empirical observations on uncrosslinked polymers.¹⁹

"MODEL" END-LINKED SILICONE NETWORK

For this work, a well-studied PDMS network was used.^{4,20,21} This network was made by reacting a vinyl-terminated poly(dimethyl siloxane) (V-PDMS) with a tetrafunctional crosslinker, tetrakis(dimethyl siloxy silane) (TDSS). If all the reactive vinyl groups were at the ends of the chain, and if each V-PDMS chain had two terminal vinyl groups, then

Table I Characterization of Network Precursors

Polymer	M_n	M_w	M_z	M_w/M_n	% Low-Mol Wt Material	
					600-6000 Range	< 450 Range
VPDMS-1 ^a	0.91	2.50	5.30	2.7	Not Detected	2.5
VPDMS-2 ^b	1.22	3.10	5.40	2.5	1.9	0.4
VPDMS-3 ^b	2.17	6.90	10.70	3.1	2.4	0.6
VPDMS-4 ^b	2.63	12.00	19.50	4.5	3.0	0.5
VPDMS-5 ^a	3.06	15.40	26.20	5.0	3.6	0.9
VPDMS-5 ^b	3.02	15.40	26.60	5.1	3.7	0.6

^a These samples analyzed as received.

^b These samples were dried under vacuum at 80°C for 60 h, then were analyzed.

an ideal network would be synthesized by reacting equal numbers of vinyl and hydride groups. Such a network would have all its network strands connected at their ends, with no dangling (i.e., elastically-ineffective) strands.

This network has other attractive features. If the vinyl and hydride groups were reacted in equimolar amounts (i.e., equal mole numbers), then the mol wt between chemically crosslinked points would be exactly equal to the number-average mol

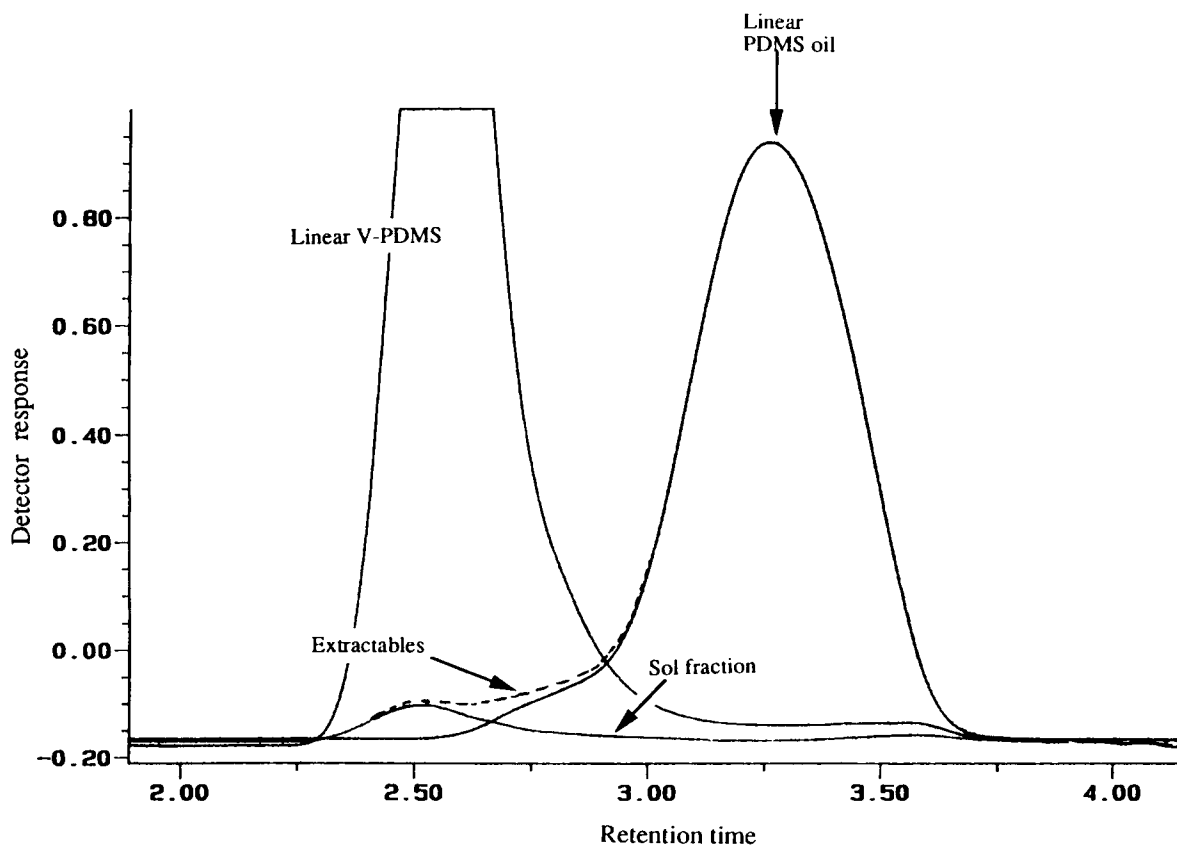


Figure 1 SEC chromatograms of linear VPDMS-4, linear PDMS diluent, and extract from PDMS network; the curve-labelled sol fraction is obtained by subtracting the area due to diluent from the area of the total extractables.

Table II Measured Properties of Silicone Networks

Sample Designation	Stoichiometric Ratio (W_x/W_p) ^a	C_x	G' at 30°C (0.1 rad/sec) Pascals $\times 10^{-5}$	dRT/M_n Pascals
VPDMS-1	0.0116	0.965	2.80	2.8×10^5
	0.0116	0.78	1.95	
	0.0116	0.60	1.20	
VPDMS-2	0.0072	0.98	2.50	2.1×10^5
	0.0072	0.80	1.92	
	0.0072	0.60	0.72	
	0.0072	0.40	0.31	
VPDMS-3	0.0035	0.985	2.02	1.16×10^5
	0.0035	0.80	1.30	
	0.0035	0.60	0.66	
	0.0035	0.40	0.24	
VPDMS-4	0.0023	0.985	1.90	9.6×10^4
	0.0023	0.80	1.17	
	0.0023	0.60	0.61	
	0.0023	0.40	0.24	
VPDMS-5	0.0019	0.985	1.00	8.4×10^4
	0.0019	0.80	0.72	
	0.0019	0.60	0.23	
	0.0019	0.40	0.085	

^a Weight of Crosslinker/Weight of VPDMS.

wt (M_n) of the V-PDMS. According to eq. (9), the modulus should be a function of the M_n of the V-PDMS as well as of the concentration of the network, C_x . We chose to vary the concentration of the network by adding an "inert" silicone oil, or trimethoxy-terminated PDMS (M-PDMS), prior to the crosslinking reaction.

The magnitudes of the moduli were then examined in light of eq. (9).

EXPERIMENTAL

Materials and Characterization

As mentioned in the previous section, the networks were prepared by reacting V-PDMSs of different M_n s with the TDSS crosslinker. The V-PDMSs were obtained from Huls-Petrarch Chemicals (Bristol, Pennsylvania) and were dried under vacuum for 60 h at 80°C, except for VPDMS-1, which was used as received. Our size exclusion chromatographic (SEC) measurements were made using a

Waters SEC, fitted with 4 Styragel columns (100, 1000, 10,000, and 100,000 Å) maintained at 31°C. Detection was by differential refractive index (DRI). SEC measurements were made on the polymers before and after the drying process; some low-mol wt material was lost ($\sim 0.1\%$ by weight). The average mol wts were virtually unaffected (see Table I).

The SEC columns were calibrated using narrow-distribution polystyrenes. To convert the polystyrene mol wts to PDMS mol wts, we used the Mark-Houwink relation for PDMS in toluene²²:

$$[\eta] = 1.36 \times 10^{-4} M^{0.69} \text{ (dL/g)} \quad (10)$$

The amount of low-mol wt material was calculated from the peak areas in the specified mol wt ranges. Most of these low-mol wt species were retained in the V-PDMS, even after drying; however, we believe any absorbed moisture was completely removed.

The crosslinker, TDSS, was analyzed by GC and was found to be 99.2% pure; it was used as received from Huls Petrarch. The catalyst was a dilute Platinum complex in low-mol wt silicone oil.

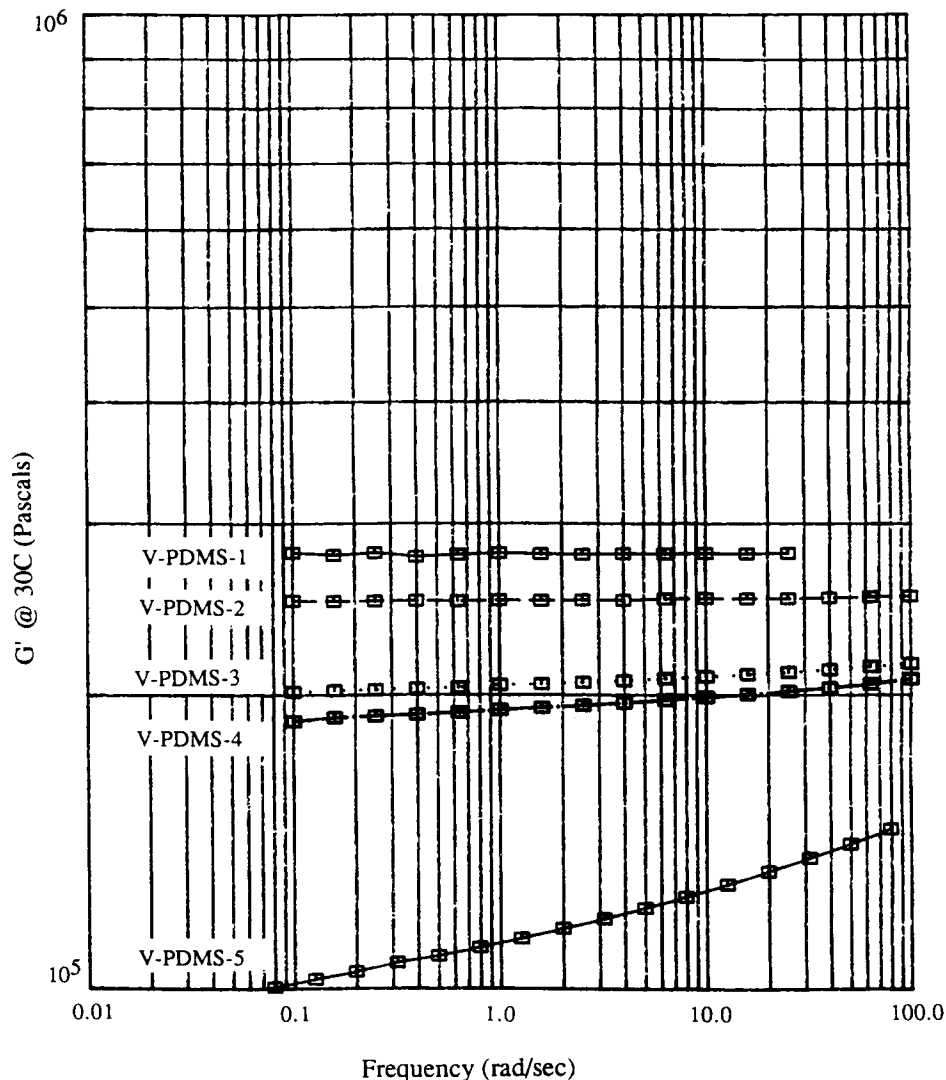


Figure 2 Elastic component, G' , of the shear modulus, plotted against frequency of oscillation. Network weight fraction = 0.98 (average). Amplitude of strain varied between 1 and 5%.

Network Preparation

All the networks that were examined in this study were prepared at stoichiometric equivalence. For each of the V-PDMSs, the stoichiometric maximum was estimated from a plot of the hardness (proportional to modulus) against the weight ratio of crosslinker to V-PDMS. This is similar to procedures reported elsewhere,²³ and ensures the preparation of networks with the minimum number of imperfections for each V-PDMS. (This does not imply the complete absence of imperfections, however).

In a typical network preparation, the V-PDMS, catalyst and diluent are mixed and degassed to form

Part A of the mixture. The crosslinker, V-PDMS, and the oil form Part B, in such proportions that when Parts A and B are mixed in equal amounts, the resulting mixture is at stoichiometric equivalence. The degassed mixture is then cast between the plates of a Rheometrics Mechanical Spectrometer (RMS-605). The top platen is lowered until contact is made with the mixture on the bottom platen. At ambient temperature, the gap is set such that the edges are slightly concave. The sample is then allowed to cure at ambient temperature for about 30 min (for samples with a high network concentration) or for 2 h (for samples with a low network concentration) before raising the temperature

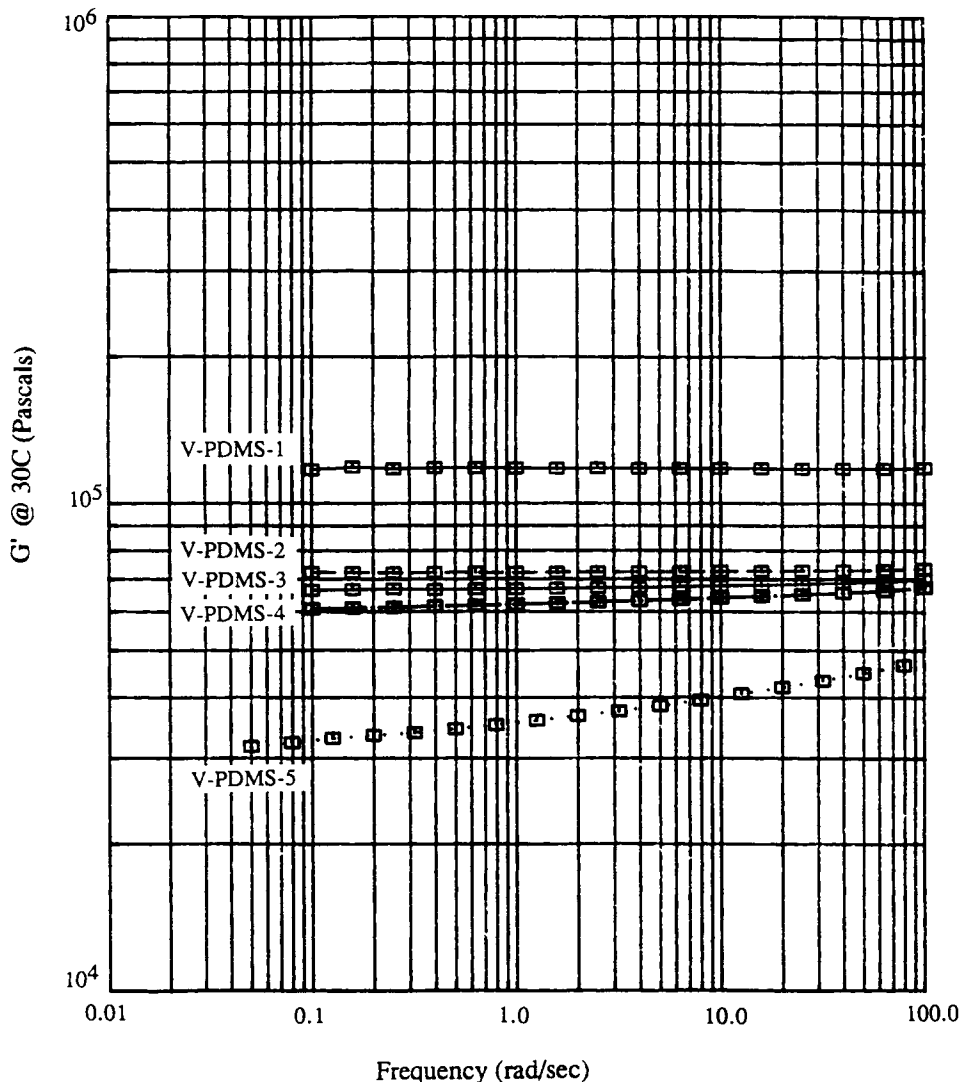


Figure 3 Same as Figure 2, for network weight fraction = 0.60. Strain amplitude varied between 5 and 15%.

to 70°C. This treatment ensures the build-up of viscosity, such that there is no overflow of the liquid mixture as the temperature is raised; it also minimizes the side reactions of the crosslinker (see Results and Discussion, below). The sample gap is readjusted at 70°C, and the cure continued for up to 15 h, or until successive G' readings, taken 30 min apart, showed less than a 1% change.

After cure, the platens were cooled to 30°C, and a frequency scan was made at strain levels sufficient to generate torques of at least 5 times the minimum measurable value.

We also estimated sol fractions by extracting the fluid from the network using hexane. By injection of hexane extract into the SEC and subtracting the

area due to the PDMS diluent (see Fig. 1), we were able to estimate sol fractions. These ranged from 1 to 5% of the network and gave us some confidence about the completeness of reaction. However, these values seem to be approximate to be used for calculations of the type outlined in the Introduction.

RESULTS AND DISCUSSION

Table II lists all the measured moduli for the networks studied.

For each V-PDMS, the network weight fractions (in this system, the weight fraction is equal to the

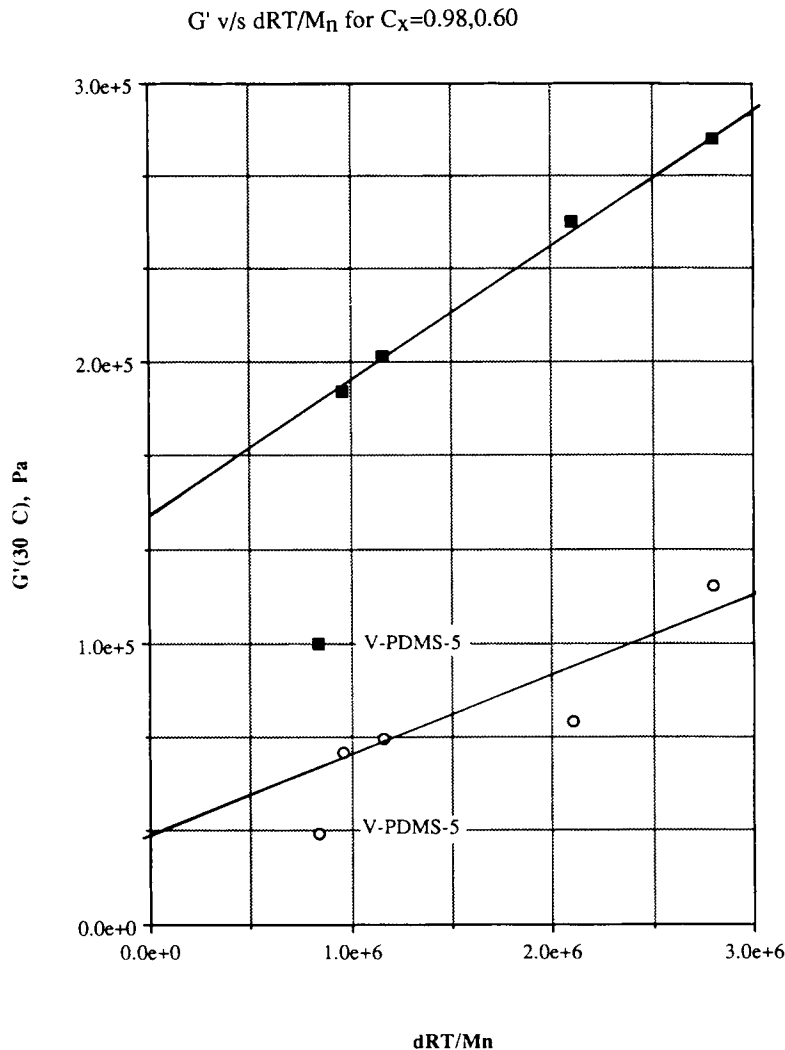


Figure 4 Plot of G' at 0.1 rad/sec and 30°C , against dRT/M_n , for networks prepared at $C_x = 0.98$ and 0.60 .

volume fraction, as the network and diluent densities are both 0.97) were chosen such that there was no syneresis during or after cure. Each of the listed networks would swell further in the diluent if exposed to it. The swelling behavior is the subject of the next article in this series.

The frequency dependence of G' , for two different network concentrations, is shown in Figures 2 and 3. (It should be mentioned that we could not prepare completely "undiluted" networks, as the catalyst was a dilute solution in M-PDMS.) For all the networks, except the ones prepared with VPDMS-5, the frequency dependence was small or negligible. Since the T_g of silicone networks was well below 30°C (literature values range from -100°C to -50°C), the frequency independence was indicative of a net-

work with few unattached chains. However, the network prepared with VPDMS-5 showed some frequency dependence. Networks, prepared with this V-PDMS, consistently behaved differently from the others. In subsequent discussions, we will refer to the errant behavior of this V-PDMS in our data analyses.

Our G' results are plotted as follows: at each network concentration (C_x), the G' value at the lowest frequency (0.1 rad/sec) is plotted against the quantity, dRT/M_n . Here, d is the network density and M_n is used as a measure of the mol wt between chemical crosslinks. Thus, this quantity is equivalent to νRT in eq. (9). According to the Dossin and Graessley³ or Valles and Macosko⁴ formalisms, the slope of such a plot should indicate affine (slope

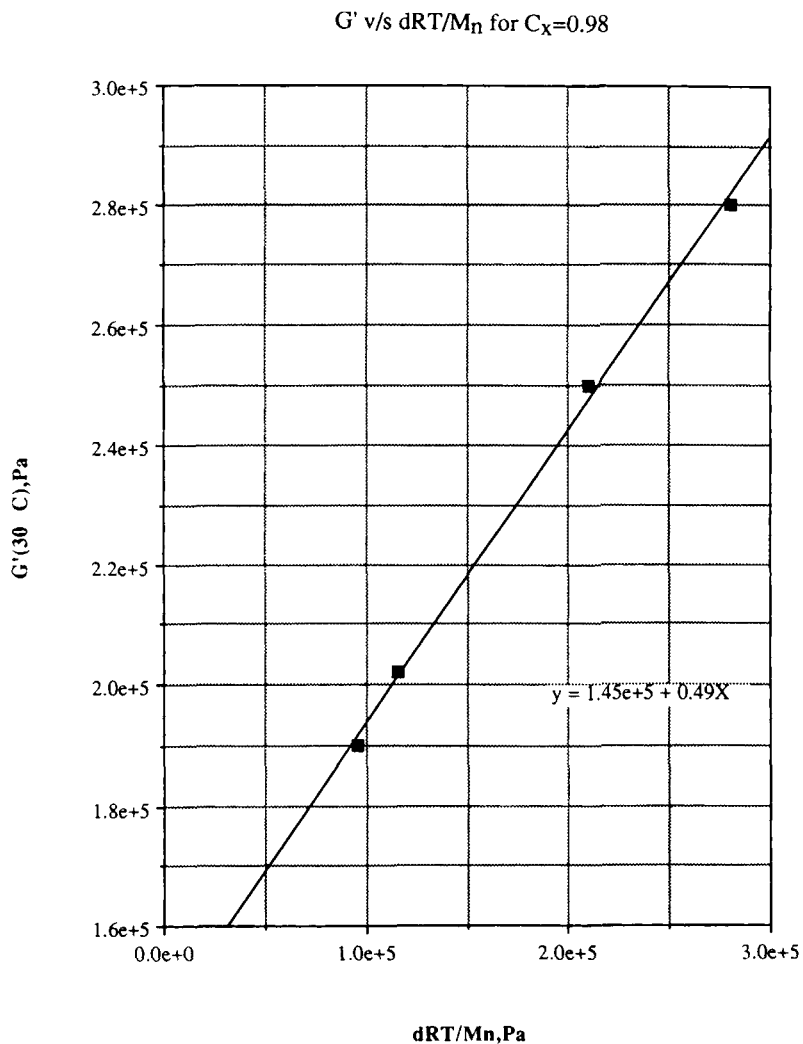


Figure 5 Same as Figure 4, but the data due to VPDMS-5 has been omitted; $C_x = 0.98$.

= 1.0) or phantom-like (slope = 0.5 for $\phi = 4$) behavior. In other words, we are estimating the factor A from:

$$G' = A(dRT/M_n) + T_e G_e^0$$

for the undiluted networks.

Also, the intercept should yield the magnitude of the plateau modulus of the linear PDMS, modified by the factor T_e , which reflects the fraction of trapped entanglements.

If these plots are made at several network concentrations, then the slope and the intercept are both functions of C_x :

$$\text{slope} = A C_x; \quad \text{intercept} = T_e G_e(C_x)$$

Figure 4 shows such a plot for all the V-PDMSs at two network concentrations. As is evident, the VPDMS-5 network deviates from expected behavior, and data for this polymer network will not be included in the subsequent analyses. Figures 5 and 6 show these plots for all concentrations for 4 networks.

Table III shows the values for the factor A , estimated from the slopes. As expected from eq. (9), all the slopes are linear in C_x , except for $C_x = 0.40$. The average value of A is 0.5, and this indicates the phantom-like nature of these networks.

The intercepts, which are the G_e values for the diluted networks, are plotted against C_x in Figure 7. The slope of the bilogarithmic plot was 2.4 and is in agreement with the value reported in the literature for a similar system.²⁴ However, the magnitude of

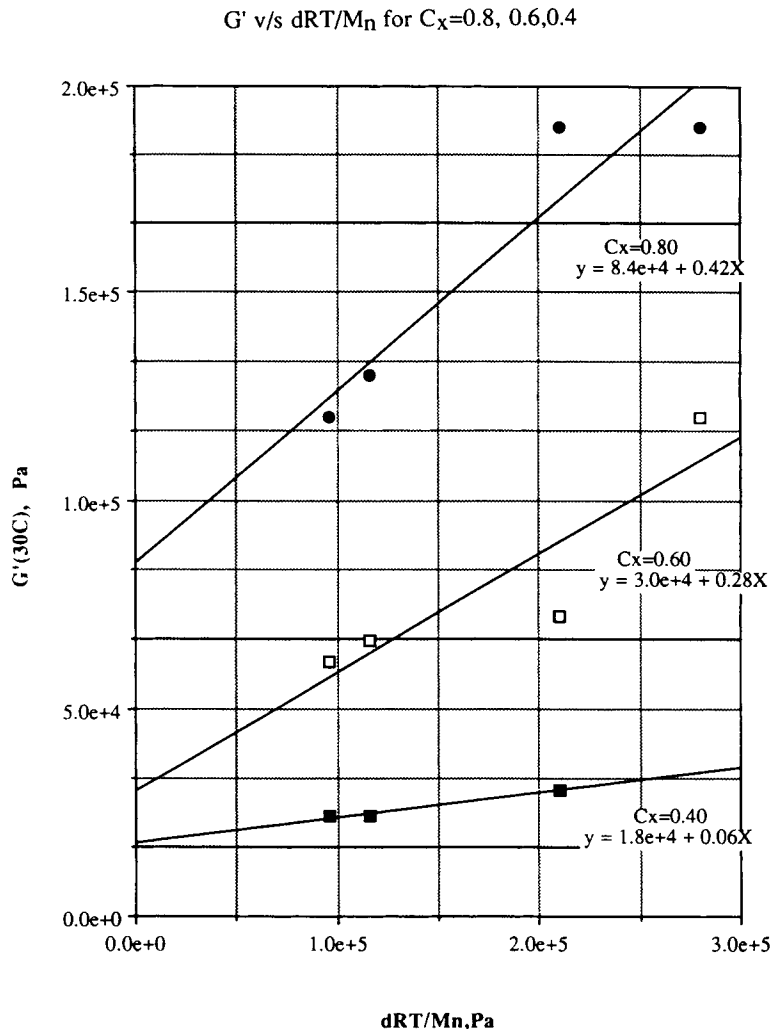


Figure 6 Elastic modulus against dRT/M_n for three other concentrations, with C_x values and line equations noted beside the respective lines.

G_e^0 estimated from these plots (intercept in Fig. 7) is 1.45×10^6 and is considerably less than the reported^{4,21,24} range of 2.0 to 2.3×10^6 for the linear and crosslinked PDMSs. This implies a T_e value of 0.6 for the undiluted network.

We believe that the deviant behavior of VPDMS-5 is due to the imperfect nature of the network formed with this polymer. Even at stoichiometric maximum, network imperfections are present, as indicated by the slope of the G' -frequency plot. We suspect that this high- M_n polymer lacks complete vinyl termination, and may contain polymers with vinyl termination only at one end. It is possible to calculate an average functionality from the location of the stoichiometric maximum (assuming that the crosslinker is tetrafunctional), and this estimate is

about 1.2 for VPDMS-5, a less than the expected value of two.

The networks with the lowest concentration ($C_x = 0.4$) also do not show the expected phantom-like

Table III Estimation of Factor A

Conc. of Network	Slope	Slope/ C_x A	Comments
0.985 ^a	0.49	0.50	Data points
0.80	0.42	0.525	from VPDMS-5
0.60	0.28	0.47	not used for
0.40	0.06	0.15	these estimates

^a Average value of actual C_x differs for each V-PDMS (see Table II).

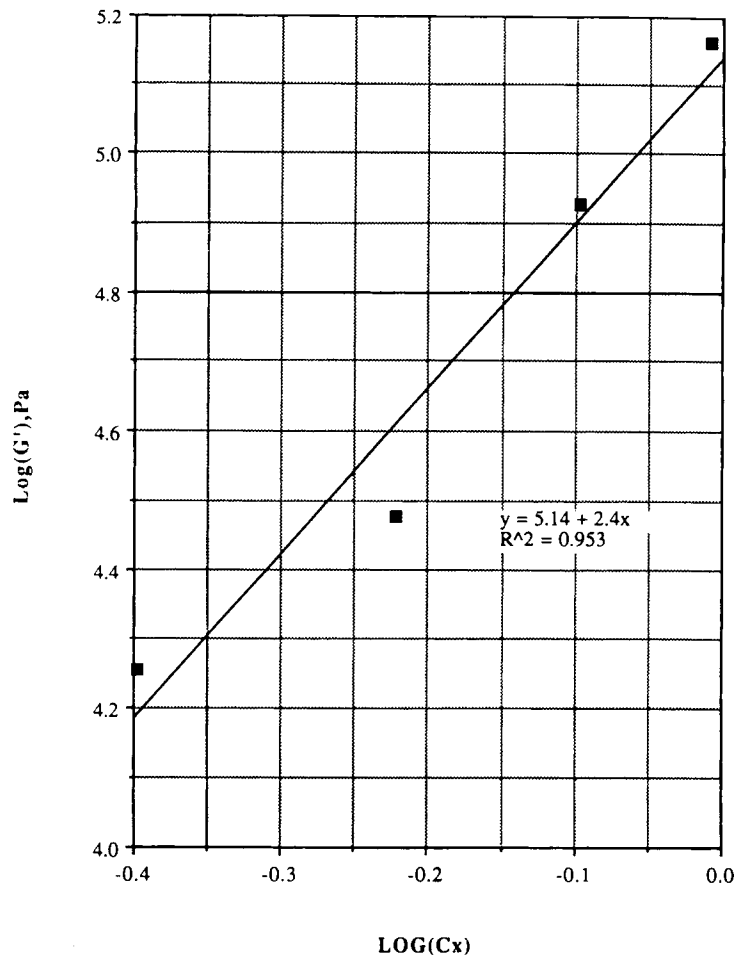


Figure 7 Intercepts of the lines from Figures 5 and 6 (at $dRT/M_n = 0$), plotted against C_x in a double logarithmic plot. Line equation and regression coefficient shown beside.

behavior in Table III. This may be attributed to side reactions that gain importance as network concentration decreases. These reactions could lead to closed loops that are elastically ineffective.²⁵ Also, the crosslinker itself is known to undergo side reactions,²⁶ especially at elevated temperatures and at low network concentrations. We have attempted to minimize these reactions by precurcuring at room temperature for 3 h, followed by a relatively low-temperature cure (70°C), but we are not certain we have eliminated the side reactions. We have also not been able to detect unreacted vinyl or hydride groups in any of the networks.

The branching theory of Miller and Macosko¹⁸ could be used to correct network imperfections, but not for side reactions. Our attempts to do so, using the measured sol fractions [using eq. (8)] yielded unacceptably high values for G_e . This could be due to errors in sol fraction estimations. Further analysis

will depend on more accurate sol fraction measurements.

CONCLUSIONS

1. End-linked PDMS networks in this study behave as phantom networks under deformations of small amplitude, with an added contribution from trapped entanglements.
2. The entanglement contribution increases as the 2.4 power of the network concentration, while the chemical crosslink factor increases linearly with concentration.
3. The fraction of trapped entanglements is less than unity.
4. For higher-mol wt VPDMSs, the degree of network imperfections (even at stoichiometric maximum) is substantial, as indicated by

the frequency dependence of G' ; an estimate of vinyl functionality for VPDMS-5 shows lack of complete vinyl termination.

5. The relation that describes the modulus behavior of these networks is:

$$G' = 0.5 \times (dRT/M_n) C_x + 1.45 \times 10^6 (C_x)^{2.4}$$

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