

Study of Crosslinking Density in Polydimethylsiloxane Networks by DSC

R. VERA-GRAZIANO,^{1,*} F. HERNANDEZ-SANCHEZ,² and J. V. CAUICH-RODRIGUEZ³

¹Instituto de Investigaciones en Materiales, UNAM, Cd. Universitaria, D. F., Apdo. Postal 70-360, Coyoacán 04510, México; ²Centro de Investigaciones Científicas de Yucatán, A. C., Apdo. Postal 87, Cordemex 97310, Mérida, Yucatán, México; ³Materials Dept./IRC, Queen Mary and Westfield College, University of London, London, U.K.

SYNOPSIS

A calorimetric study for estimating crosslinking densities of polydimethylsiloxane (PDMS) networks is presented. It involves the experimental determination of the heat capacities of the polymer with (C_p^i) and without (C_p^0) crosslinking. The theoretical basis of the method is described as well as the procedure used for the determination of the C_p s. The crosslinking densities of PDMS networks, determined by absorbency (swelling) measurements, using the Flory-Rehner equation, and by the method described here, are compared. The PDMS, obtained by the anionic synthesis of octamethylcyclotetrasiloxane, was analyzed by gel permeation chromatography and infrared spectroscopy. Separate samples of the polymer were further crosslinked at different network densities. The C_p s and the thermal stabilities were determined by DSC and TGA, respectively. The results indicate that the crosslinking density ratios of the polymer networks calculated by the relation $\Delta C_p^i/C_p^0$ are in reasonable agreement with those obtained from absorbency measurements. The crosslinking density can also be obtained from heat capacity measurements if the density of the network is known at the temperature that ΔC_p is obtained. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The crosslinking density in polymer networks is usually estimated throughout solvent absorbency (swelling) measurements.^{1,2} The absorbency, A , is defined as

$$A = (P_h - P_s)/P_s \quad (1)$$

where P_s and P_h are the weights of the dry and the swollen polymer gel in equilibrium conditions, respectively.

Before P_s is determined it is necessary to eliminate both the non-crosslinked material, by extraction, and the solvent, by drying; otherwise non-reproducible results are obtained because during swelling, chain molecules diffuse into the solvent at different rates, depending on their size. Loss of ab-

sorbed solvent (by leaking or evaporation) during the weighting of the swollen specimens may also introduce significant errors.

The crosslinking yield (also known as effective crosslinking), X_y , and the weight loss, L_w , are:

$$X_y = (P_s/P_i) \quad (2)$$

$$L_w = (P_i - P_s)/P_i \quad (3)$$

where P_i is the weight of the dried polymer before swelling and extraction and $(P_i - P_s)$ is the weight of the non-crosslinked material.

Calculation of the crosslinking density by absorbency measurements requires the determination of the volume fraction of the polymer in the swollen mass, v_2 , the knowledge of the molar volume of the solvent, V_1 , and the Flory-Huggins polymer-solvent interaction parameter, χ_1 . Such is the case when the Flory-Rehner,¹ eq. (4), or other similar equations are used:

$$n^{FR} = -[v_2 + v_2^2\chi_1 + \ln(1 - v_2)]/V_1(v_2^{1/3} - 0.5v_2) \quad (4)$$

* To whom correspondence should be addressed.

where n^{FR} is the number of active network chain segments (in mols per unit volume). The term n^{FR} equals ρ/M_c , where ρ is the density of the polymer and M_c the molecular weight of a crosslinked segment.

Some factors need to be considered before the final numerical result is accepted: the "front factor", r_i^{-2}/r_0^{-2} , (relation of unstrained, r_i^{-2} , to most probable end-to-end, r_0^{-2} , distances in the network) not explicitly expressed in eq. (4) may be significantly different from unity,³ and deviations from the "statistical network" may lead to swelling volumes up to 20% less than theoretically predicted.⁴

An alternative method for estimating the crosslinking density, based on the change in the heat capacity of the polymer by crosslinking, is described below.

THEORY

Heat Capacity and Crosslinking Density

The degrees of freedom of a linear amorphous polymer depend strongly upon its condensed state: glassy (below $T_g - 40^\circ\text{C}$), elastomeric region (between $T_g - 30^\circ\text{C}$ and T_g), viscoelastic liquid (between T_g and $T_g + 50^\circ\text{C}$) and the liquid state (about $T_g + 60^\circ\text{C}$).

The degrees of freedom, f , for an amorphous polymer in the liquid state can be approximated by⁵:

$$f = 3 \sum_{i=1}^n N_i \gamma_i \quad (5)$$

where $\sum_{i=1}^n N_i$ is the total number of molecules in the polymer mass, N_i is the number of molecules of molecular weight M_i , and γ_i is the number of atoms in each molecule of molecular weight M_i . Equations (5) to (12) do not consider the internal degrees of freedom (electronic) of the atoms because that reticular part, associated to vibration of atoms, is relevant only in crystalline systems.⁶

The value of f decreases to f_g from the liquid to the glassy state:

$$f_g = 3 \sum_{i=1}^n N_i \gamma_i - 3 \sum_{i=1}^n N_i' \gamma_i' \quad (6)$$

where the second term of the right-hand side of eq. (6) represents the degrees of freedom lost by all kinds of physical linkings of the chain segments: van der Waals forces, entanglements, etc.

For a linear amorphous polymer that has been crosslinked, the value of f , in the glassy state, is further reduced to f_{gc} :

$$f_{gc} = 3 \sum_{i=1}^n N_i \gamma_i - 3 \sum_{i=1}^n N_i' \gamma_i' - 3 \sum_{i=1}^n N_i'' \gamma_i'' \quad (7)$$

where the third term of the right-hand side of eq. (7) represents the degrees of freedom lost by the chemical bonding of the chain segments.

Well above T_g , the second term of the right-hand side of eq. (7) disappears and f becomes f_c :

$$f_c = 3 \sum_{i=1}^n N_i \gamma_i - 3 \sum_{i=1}^n N_i'' \gamma_i'' \quad (8)$$

From the mechanical point of view, a polymeric system in the liquid state, eq. (5), can be considered as a set of independent oscillators, each one corresponding to one normal vibration.⁷ The heat capacity, C_p , of linear amorphous polymers in the liquid state, can be related to the degrees of freedom and the temperature, T , through the Debye approximations^{6,8}

$$C_p = f \phi \left(\frac{\theta}{T} \right)_i \quad (9)$$

where θ is the Debye's temperature and is equal to $\bar{h}w_m$. Here \bar{h} is the Plank constant and w_m is the minimum frequency at which all atoms are excited. So θ depends upon the specific characteristics of the material,

$$\phi \left(\frac{\theta}{T} \right)_i = \left[D_i \left(\frac{\theta}{T} \right) - \frac{\theta}{T} \frac{\delta D_i(\theta/T)}{\delta(\theta/T)} \right] \quad (10)$$

The Debye function, $D_i \left(\frac{\theta}{T} \right)$, is given by

$$D_i \left(\frac{\theta}{T} \right) = \frac{3}{\left(\frac{\theta}{T} \right)^3} \int_0^{\theta/T} \frac{Z_i^3 dZ_i}{e^{Z_i} - 1} \quad (11)$$

where Z_i is equal to $(\bar{h}w_i/T)$. The temperature T is expressed in energetic units KT_0 , where T_0 is the absolute temperature, K is the Boltzmann constant, and w_i is the vibration frequency of the i element.

If the degrees of freedom in the liquid state are restricted by crosslinking, the C_p will change to:

$$C_p = f_c \phi \left(\frac{\theta}{T} \right)_i \quad (12)$$

For a given system, $\phi\left(\frac{\theta}{T}\right)_i$ remains invariant at constant temperature. So under these conditions C_p will only depend upon f_c .

The crosslinking density can now be related to the heat capacity in the following way. The crosslinking density, ρ_c , was defined by Flory⁹ as the number of crosslinked segments (in mols), ν , divided by the total number of segments (in mols), N_0 , and each polymer material has a given number of N_0 segments. If both quantities are expressed in terms of unit volume, then:

$$\rho_c = \frac{\nu}{N_0} = \frac{\nu/V}{N_0/V} = \frac{n^{FR}}{N_{0V}} \quad (13)$$

where ν/V is the total number of crosslinked segments per unit volume, so it equals n^{FR} , and N_{0V} is the total number of segments per unit volume (both in mols/cm³). Equation (13) always yields ρ_c values less than 1 because not all chain segments are chemically crosslinked.

However, if we redefine the total number of segments as those with real possibility of being crosslinked, N_c , and N_{cV} as N_c/V , then the following crosslinking density, ρ'_c , may theoretically reach the unity:

$$\rho'_c = \frac{\nu/V}{N_{cV}} = \frac{n^{FR}}{N_{cV}} \quad (14)$$

The quantity ν is equivalent to the number of chemical bonds that lead to network formation. Subtracting eq. (5) from eq. (8), the degrees of freedom lost by crosslinking is obtained:

$$f_c - f = -3 \sum_{i=1}^n N_i'' \gamma_i'' \quad (15)$$

where the right-hand side term of eq. (15) equals the number of crosslinked segments, ν , for the network well above T_g .

The degrees of freedom obtained when chemical crosslinking occurs at all points with real possibility of being crosslinked is equal to the result of subtracting eq. (5) from eq. (6):

$$f_g - f = -3 \sum_{i=1}^n N_i' \gamma_i' \quad (16)$$

So, the right-hand side term of eq. (16) equals N_c .

The result of dividing eq. (15) by eq. (16) is similar

to that obtained by rearranging and dividing eqs. (8) and (6),

$$\frac{f_c - 3 \sum_{i=1}^n N_i \gamma_i}{\sum_{i=1}^n N_i \gamma_i} = \frac{3 \sum_{i=1}^n N_i'' \gamma_i''}{3 \sum_{i=1}^n N_i' \gamma_i'} \quad (17)$$

The right-hand side term of eq. (17) equals our definition of ρ'_c , according to eq. (14), because:

$$\frac{3 \sum_{i=1}^n N_i'' \gamma_i'' / V}{3 \sum_{i=1}^n N_i' \gamma_i' / V} = \frac{\nu/V}{N_{cV}} = \rho'_c \quad (18)$$

In this way, the crosslinking density can be related to the degrees of freedom of the amorphous crosslinked polymer well above T_g .

As mentioned above, the heat capacity is the product of the degrees of freedom and the Debye term, so if the left-hand side term of eq. (18) is multiplied and divided by $\phi(\theta/T)$ then ρ'_c can be expressed in terms of the heat capacities:

$$\rho'_c = \frac{3 \sum_{i=1}^n N_i'' \gamma_i'' \phi\left(\frac{\theta}{T}\right)_i}{3 \sum_{i=1}^n N_i' \gamma_i' \phi\left(\frac{\theta}{T}\right)_i^0} = \frac{C_p^i - C_p^0}{C_p^0} = \frac{\Delta C_p^i}{C_p^0} \quad (19)$$

where C_p^i and C_p^0 are the heat capacities of the polymer network at a given crosslinking density, $(\rho'_c)_i$, and that of the non-crosslinked polymer, respectively. Then, ν should be proportional to ΔC_p . The C_p s can be properly obtained by differential scanning calorimetry (DSC) as described below.

Determination of Heat Capacities

The experimental determination of heat capacities by DSC is usually done by the following method of height differences. First, three thermograms are obtained in a given range of temperatures, all at the same heating rate: the baseline, B , of the DSC cell; the baseline of a reference sample, R (pure sapphire or aluminum oxide); and the thermogram of the sample, S . Then the C_p of the sample at a given temperature is obtained by the height differences relation:

$$C_p = \frac{S - B}{R - B} \quad (20)$$

However, according to our experience, this method provides only approximate results.

The definition of heat capacity (amount of heat per unit mass required to raise the temperature one degree) is used here to obtain the C_p s by DSC measurements.¹⁰ Such determinations are made in the following way:

The temperature of the sample is instantaneously raised one degree (from T_x to T_{x+1}). The area limited by the curve and the baseline, between T_x and T_{x+1} , is the heat capacity, in accordance with the above definition.

Determinations of this type can be properly done in DSC equipment with very small thermal inertia, so that in the elapsed time the sample absorbs only the required energy to raise its temperature just one degree.

The described method of areas to obtain the C_p s is more complicated than the method of height differences but is more accurate.^{11,12}

Relations for Crosslinking Densities

The absolute values of crosslinking density obtained by eqs. (4) and (19) are expected to be different because in the first case n^{FR} is given in terms of number of active network chains per unit volume (mol/cm^3), while in the second case ρ'_c equals n^{FR}/N_c and experimentally is obtained as a relation of heat capacities [(Cal/(g K))/Cal/(g K)].

However, ρ'_c can be related to n^{FR} by taking two samples, x and y , of the same polymer with different degrees of crosslinking and dividing them. From eq. (13):

$$\frac{(\rho'_c)_x}{(\rho'_c)_y} = \frac{\left(\frac{v/V}{N_0}\right)_x}{\left(\frac{v/V}{N_0}\right)_y} = \frac{n_x^{FR}}{n_y^{FR}} \quad (21)$$

In a similar way, by dividing $(\rho'_c)_x$ and $(\rho'_c)_{y'}$ as given by eqs. (14) and (19):

$$\frac{(\rho'_c)_x}{(\rho'_c)_{y'}} = \frac{\left(\frac{v/V}{N_c}\right)_x}{\left(\frac{v/V}{N_c}\right)_y} = \frac{n_x^{FR}}{n_y^{FR}} = \frac{\Delta C_p^x/C_p^0}{\Delta C_p^y/C_p^0} = \frac{\Delta C_p^x}{\Delta C_p^y} \quad (22)$$

The crosslinking density from heat capacity measurements, n_e , can be calculated as follows:

$$n_e [\text{mol}/\text{cm}^3] = \frac{\Delta C_p \times \rho}{C_p^{\text{mol}}} \left[\frac{\frac{\text{Cal}}{\text{g K}} \times \frac{\text{g}}{\text{cm}^3}}{\frac{\text{Cal}}{\text{mol K}}} \right] \quad (23)$$

where C_p^{mol} is the heat capacity in Cal/(mol K), and ρ is the density of the material in g/cm^3 . Both, C_p^{mol} and ρ , will change with crosslinking density and with temperature.

The data obtained by swelling and heat capacity measurements can be used to compare crosslinking density ratios, eqs. (21) and (22), and crosslinking densities, eqs. (4) and (23), respectively.

EXPERIMENTAL

Materials

The monomer, octamethylcyclotetrasiloxane, D_4 (Huls Petrarch Systems), was dehydrated before use with LiH and then distilled. Previously dried KOH (from Aldrich), mesh 60, was used for the anionic polymerization of D_4 . Benzoyl peroxide and H_2SO_4 were used to crosslink the polydimethylsiloxane (PDMS) at different crosslinking levels.

Procedures

The polymer was obtained in a two-step reaction. First, the synthesis of the initiator: potassium silanolate. It was made by the following procedure: stoichiometric amounts of D_4 and KOH were mixed by stirring under dry N_2 atmosphere in a glass reactor. The reaction was set at 110°C under reflux for 1 h. The silanolate was quenched below 0°C under N_2 and kept under those conditions for further use. The second step was the anionic polymerization of D_4 : the monomer was refluxed at 100°C under N_2 atmosphere and the initiator was added into the reactor, keeping the same conditions for 1.5 h. The polymerization reaction was terminated by adding methanol.^{13,14}

The obtained polymer was characterized by infrared spectroscopy (Perkin-Elmer spectrophotometer, model 683) in chloroform solution at 1% concentration, and by gel permeation chromatography (GPC) (Waters model 150 C) in toluene.

The PDMS was crosslinked by a hydrogen atom abstraction reaction with the peroxide-derived radical, succeeded by polymeric radical coupling as follows: the PDMS was mixed with benzoyl peroxide at 2% concentration and catalytic amounts of H_2SO_4 under vacuum. The temperature was risen to 110°C

to start the reaction. Crosslinking density was controlled by the reaction period: from 2 to 6 h. The crosslinking reaction was terminated by adding benzene in excess.

The samples were subjected to extraction with benzene, to eliminate the non-crosslinked material, and dried to constant weight. Crosslinking densities were determined by eqs. (4) and (19). The interaction parameter, χ_1 , used in eq. (4) is equal to 0.744 for the PDMS-benzene pair.

DSC thermograms (Perkin-Elmer, DSC-2C) were obtained as a function of temperature, at a heating rate of 10°/min, and as a function of time at different constant temperatures. TGA measurements (Perkin-Elmer TGS-2) were also made to determine the stability of the materials as a function of temperature and crosslinking. The C_p s were calculated from the thermograms by the method of areas described above.

RESULTS AND DISCUSSION

Chemical Reactions

The polymerization reaction was monitored by IR as depicted in Figure 1, where the spectra of D_4 is compared with that of the obtained PDMS. The intensity of the D_4 band at 1263 cm^{-1} , corresponding to the CH stretch vibrations of methyl groups on

Si, decreases as the polymerization proceeds. The 1263 cm^{-1} band is always accompanied by one or more equally intense bands, ranging from 763 to 847 cm^{-1} , which arise from methyl rocking and Si-C stretch vibrations. This region gives useful information about the structure of the molecule. Two methyls on Si absorb at the 855–800 cm^{-1} region. As it can be observed (Fig. 1), the two methyl groups of D_4 absorb differently than those of PDMS in that region. D_4 has a non-planar structure, and probably it is an unstrained structure, but some degeneration of the methyl rocking vibration may occur.¹⁴

Also, the 1076 cm^{-1} band, arising from an asymmetric Si-O-Si stretch vibration in D_4 , splits into two overlapping components in progressively longer chain compounds, with points of maximum absorption at 1020 cm^{-1} and 1087 cm^{-1} , as shown in Fig. 1.

The obtained PDMS was a transparent liquid. Because the polymerization reaction was terminated at a 50% yield, no high-molecular-weight polymer (viscoelastic solid) was obtained.

In general, conversion of cyclosiloxanes to polysiloxanes takes place without the formation of any new type of chemical bonds; and because the bond energy in the cyclic compound (D_4) is about the same as that of the polymer, the polymerization reactions are thermodynamically controlled through entropy changes. During polymerization of D_4 , depropagation and redistribution reactions are significant, so

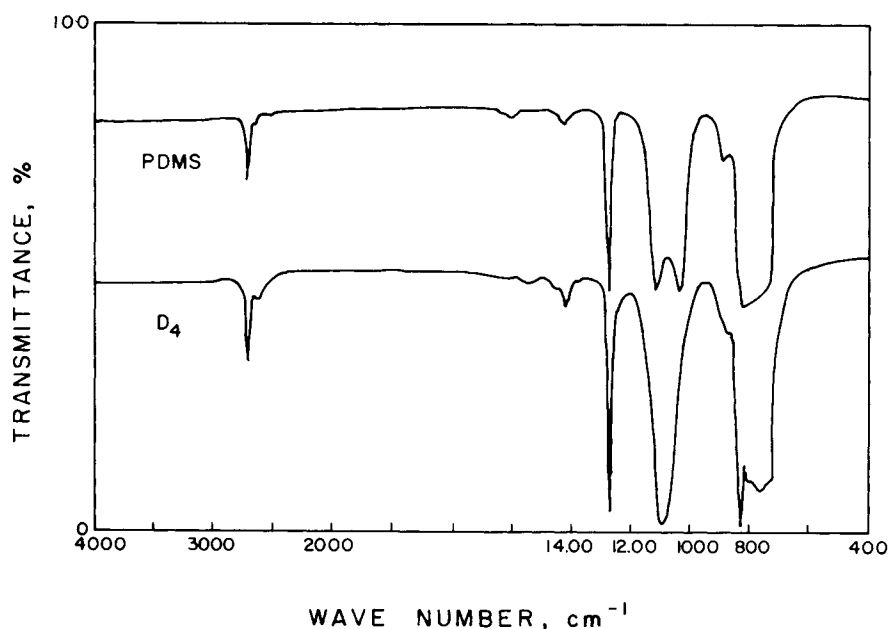


Figure 1 Infrared spectra of octamethylcyclotetrasiloxane, D_4 , and polydimethylsiloxane, PDMS.

Table I Molecular Weights and Polydispersity of Polydimethylsiloxane Obtained by Anionic Polymerization of D_4

Reaction Time, min.	Number Average Molecular Weight M_n^-	Weight Average Molecular Weight M_w^-	Polydispersity M_w^-/M_n^-
20	66,030	83,391	1.26
30	58,102	104,718	1.53
50	64,142	115,376	1.79

formation of macrocyclics is common but crosslinking is not.¹⁴ Molecular weight control may be obtained by the reaction time or by adding a chain transfer agent.

Depropagation reactions lead to low molecular weight linear siloxanes as shown below. It should be mentioned that fluid PDMS have number average molecular weights, M_n^- , up to 430,000, corresponding to about 5850 repeating units. Typical average molecular weights, M_w^- , of the obtained PDMS, as determined by GPC, were about 115,000 (about 1550 repeating units) with a polydispersity (M_w^-/M_n^-) of about 1.80, as shown in Table I.

Several reports show that the molecular weight distribution of PDMS, prepared from D_4 and potassium silanolate, becomes broader as the polymerization proceeds; typical polydispersity is about 2.0.¹⁴ In the range of high molecular weights, M_w^- increases with polymerization time but M_n^- remains fairly constant throughout the polymerization.

Crosslinking of the PDMS was properly obtained at acid concentrations below 0.1% (w). The minimum reaction time for effective crosslinking was set in 2 h, as it was checked by swelling experiments in benzene. Before that time, some crosslinking involving two (or probably three) chain molecules could take place but no gels were detected.

Absorbency

As expected, the absorbency A , of the PDMS networks decreased inversely with crosslinking reaction time, the amount of extractable material (loss of weight) decreased, and the crosslinking yield (X_y) increased, as shown in Table II. Both, A and X_y behaved linearly with reaction time up to 4 h, then the rate of reaction decreased and so did A and X_y . The crosslinking density, as determined by eq. (4), also increased with reaction time (Table II). These data will be discussed below.

Thermal Stability

The thermal stability of the crosslinked PDMS, as determined by TGA, is much higher than that of the non-crosslinked polymer, as shown in Figure 2. The non-crosslinked liquid polymer loses weight above 100°C (373 K), suggesting the presence of low molecular weight siloxanes; while for the crosslinked PDMS it initiates above 425°C (698 K). It can also be observed that thermal stability increases with the crosslinking level.

To ensure the efficiency of extraction, the data in Figure 2 was compared with the boiling points of low molecular weight siloxanes (Table III).¹⁵ It can

Table II Crosslinking Data for PDMS Networks Obtained by Absorbency Measurements

Reaction Time, h	Absorbency, A g/g Eq. (1)	Crosslinking Yield, X_y % Eq. (2)	Crosslinking Density, n^{FR} mol/cm ³ Eq. (4)	Average Molecular Weight of Chain Segment, M_c $M_c = \rho/n^{FR}$
0	—	0.0	0.00	115,000
2	4.45	26.6	1.44×10^{-4}	6,812
4	3.11	56.7	2.01×10^{-4}	4,945
6	2.87	68.4	2.25×10^{-4}	4,498
8	2.24	80.3	2.43×10^{-4}	

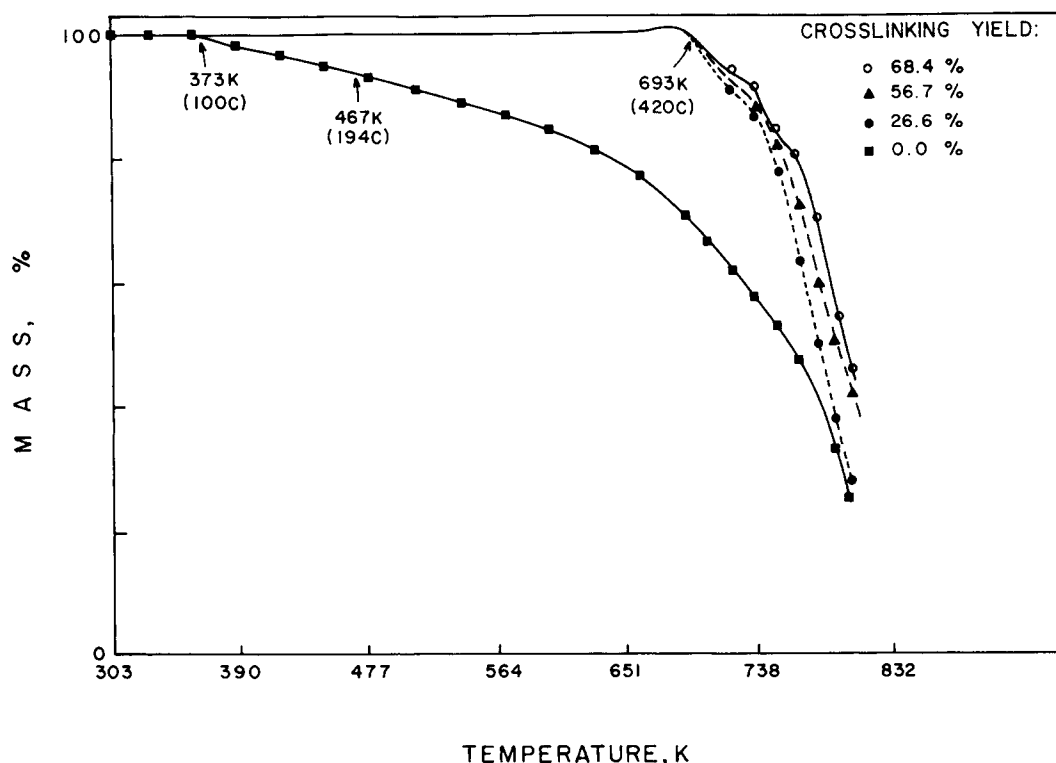


Figure 2 TGA thermograms of polydimethylsiloxane at different crosslinking yields.

be deduced that no D_4 , neither di, tri, or tetramer, was present in significant amounts in the crosslinked polymers after the extraction, otherwise weight losses would be observed near the corresponding boiling temperatures. However, in the non-crosslinked PDMS, hexamethyldisiloxane (bp 373 K) and other low molecular weight siloxanes were probably present.

DSC Study

The DSC thermograms (Fig. 3) show that $\Delta H/\Delta T$ increases with temperature but, at any constant temperature, $\Delta H/\Delta T$ shows lower values as the degree of crosslinking increases. It means that as

crosslinking density increases, more heat (temperature) is required to reach the same segment mobility. This behavior suggests that the mobility of crosslinked segments decreases as their length decreases.¹⁶

The heat capacity, C_p , is temperature dependent.⁶ Figure 4 shows that for the crosslinked PDMS, the absorbed heat related to C_p increases with temperature. Also, at constant temperature, the C_p generally decreases as the degree of crosslinking increases, as in the case of the crosslinked PDMS (Fig. 5). This behavior agrees with that shown in Figure 3 because the absorbed heat decreases as the crosslinking density increases.

The heat capacities obtained experimentally and

Table III Boiling Temperatures of Low Molecular Weight Siloxanes¹⁵

Substance	Boiling Point, K (C)	Molecular Weight
Decamethyltetrasiloxane: $[(CH_3)_3SiOSi(CH_3)_2]_2-O$	467 (194)	310.7
Octamethylcyclotetrasiloxane (D_4): $[(CH_3)_2SiO]_4$	448 (175)	296.6
Octamethyltrisiloxane: $(CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_3$	425 (152)	236.4
Hexamethyldisiloxane: $(CH_3)_3SiOSi(CH_3)_3$	373 (100)	162.4

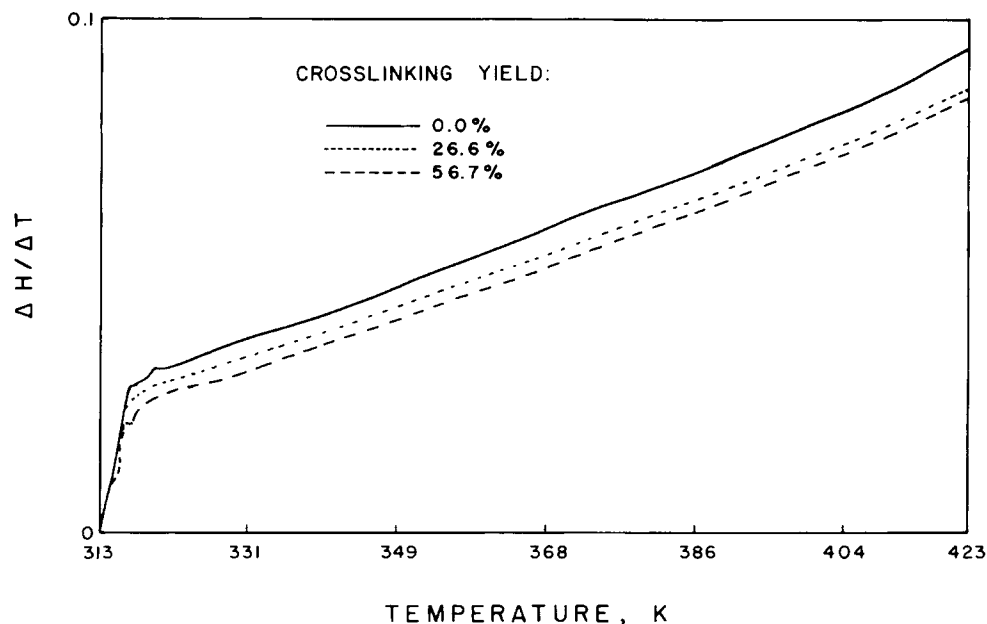


Figure 3 DSC thermograms of polydimethylsiloxane at different crosslinking yields.

the crosslinking densities calculated by eq. (19), both at three different temperatures, are shown in Table IV. As expected, the C_p s decrease with crosslinking reaction time and are temperature dependent. However, the $(\rho'_c)_i$ increase with reaction time but are almost temperature independent.

As mentioned above, the values of $(n^{FR})_i$ and $(\rho'_c)_i$ are different (see Tables I and IV, respectively). However, the corresponding crosslinking density ratios obtained by eqs. (21) and (22) are similar (see

Table V) although the values obtained by eq. (22) are higher.

It can be observed in Table V that the $(\rho'_c)_x/(\rho'_c)_y$ values are temperature dependent; they decrease slightly with temperature from 314 K to 354 K, but at 434 K the difference is significant. This result calls for a deeper interpretation, but our hypothesis is that it is related to a significant increment in chain mobility at high temperatures, including a reduction in van der Waals forces. The

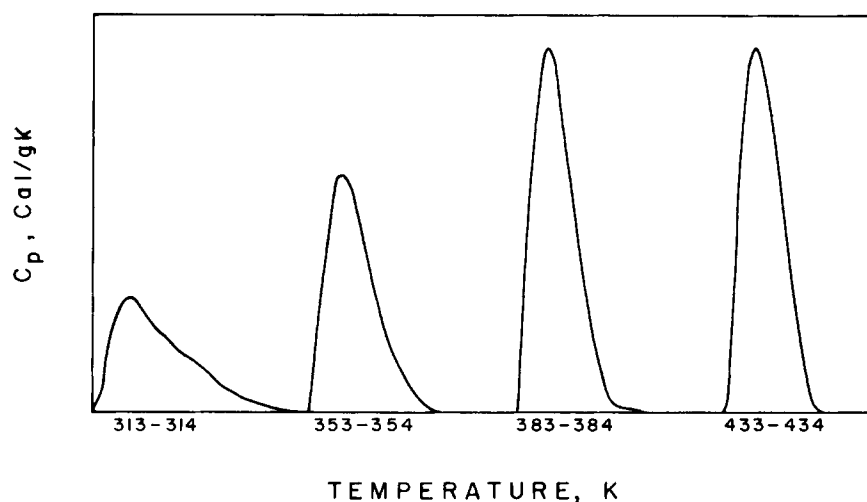


Figure 4 Heat capacity, C_p , of crosslinked polydimethylsiloxane (56.7% yield) at different temperatures.

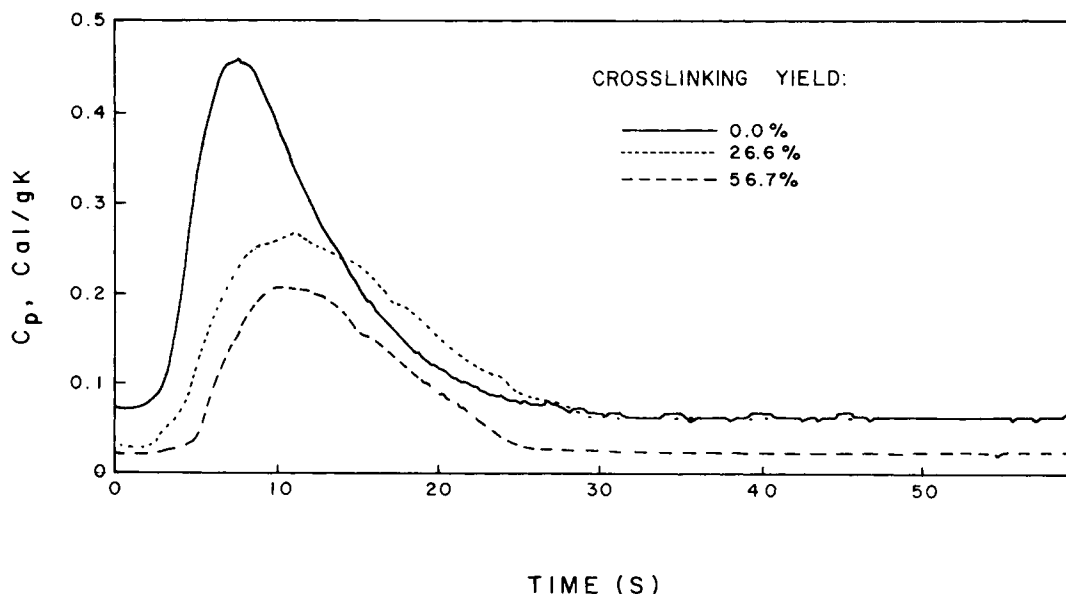


Figure 5 Heat capacity, C_p , of polydimethylsiloxane at different crosslinking yields, temperature 314 K.

third column of Table V shows corrected results at 314 K after they were obtained by eq. (21).

The values of n_e , calculated by eq. (23), as well as ΔC_p and C_p^{mol} , are shown in Table VI. A reasonable agreement can be observed between the crosslinking densities obtained by the Flory-Rehner equation (Table II) and those obtained by the heat capacity method (Table VI) described in this study. Again, the values obtained by eq. (23) are higher than those obtained by eq. (4).

The observed differences in the crosslinking densities, as obtained by absorbency and heat capacity measurements, require further interpretation. But they may be attributed to deviations from the unity in the "front factor" of the PDMS network, or to differences between the obtained PDMS network and the "statistical network."^{3,4}

CONCLUSION

This study, based on fundamental principles, shows that the heat capacity can be used for estimating crosslinking densities of PDMS networks. The calorimetric method provides fine enough data to differentiate crosslinking levels in PDMS networks. In order to obtain reproducible data, it is necessary to use DSC equipment with low thermal inertia.

In order to calculate the crosslinking density from heat capacity measurements, C_p^{mol} and ρ must be known for the temperature at which ΔC_p is obtained. Both the values of crosslinking density ratios and the crosslinking densities of PDMS networks, obtained by absorbency and heat capacity measurements, respectively, show a reasonable agreement, although the values yielded by absorbency are lower.

Table IV Heat Capacities and Related Crosslinking Data of PDMS Networks

Reaction Time, h	Heat Capacity, Cal/g K			Crosslinking Density, ρ'_c , Eq. (19)		
	314 K	354 K	434 K	314 K	354 K	434 K
0	0.288	0.396	0.567	0.00	0.00	0.00
2	0.258	0.357	0.494	0.1042	0.0985	0.1287
4	0.240	0.332	—	0.1667	0.1616	—
6	0.225	0.311	—	0.2188	0.2146	—

Table V Crosslinking Density Ratios of PDMS Networks

Reaction Time Relation, x/y $x > y$	Crosslinking Density Ratio				
	$(\rho_c)_x/(\rho_c)_y$ (Eq. 21)		$(\rho'_c)_x/(\rho'_c)_y$ (Eq. 22)		
	A ¹ 300 K	B ² 314 K	314 K	354 K	434 K
6 h/2 h	1.672	1.802	2.101	2.178	—
4 h/2 h	1.456	1.527	1.600	1.639	2.410
6 h/4 h	1.148	1.189	1.312	1.328	—

¹ Without correction.² With density and temperature correction**Table VI Crosslinking Data for PDMS Networks Obtained by Heat Capacity Measurements**

Reaction Time, h	ΔC_p , at 314 K Cal/(g K)	C_p^{mol} , ¹ Cal/ (mol K)	Calculated Crosslinking Density, n_e , mol/cm ³ Eq. (23)
0	—	—	—
2	0.030	189.8	1.56×10^{-4}
4	0.048	225.6	2.10×10^{-4}
6	0.063	266.1	2.37×10^{-4}

¹ Estimated from M_c , Table II.

NOMENCLATURE

A	Absorbency, g/g.
P_h	Weight of swollen polymer gel, g.
P_s	Weight of dried polymer after extraction, g.
X_y	Crosslinking yield, g/g.
L_w	Weight loss percent, g/g.
v_2	Volume fraction of the polymer, in the swollen mass, cc/cc.
V_1	Molar volume of the solvent, mols/cc.
χ_1	Flory-Huggins polymer-solvent interaction parameter.
n^{FR}	Flory-Rehner crosslinking density, eq. (4), mols/cc.
n_e	Crosslinking density, calculated by eq. (23), mols/cc.
ρ_s	Density of solvent, g/cc.
ρ	Polymer density, g/cc.
ρ_c	Crosslinking density, calculated by eq. (13), mols/mol.

ρ'_c	Crosslinking density, calculated by eq. (14), mols/mol.
M_c	Molecular weight of a crosslinked segment, mols/(mol-g).
r_i^{-2}	Square of unstrained end-to-end distance.
r_0^{-2}	Square of most probable end-to-end distance.
f	Degrees of freedom in the liquid state.
γ_i	Number of atoms in each molecule of molecular weight M_i .
N_i	Number of molecules of molecular weight M_i .
N_0	Total number of segments, mols.
N_{0V}	Total number of segments per unit volume, mols/cc.
N_c	Total number of segments with real possibility of being crosslinked, mols.
N_{cV}	Total number of segments per unit volume with real possibility of being crosslinked, mols/cc.
C_p	Heat capacity, Cal/(g K).
C_p^{mol}	Heat capacity, Cal/(mol K).
T	Temperature, K.
T_g	Glass transition temperature, K.
K	Boltzmann constant.
ϵ_i	Interaction energy of a molecule with molecular weight i .
h	Plank constant.
w	Frequency at which the atoms are excited.
w_m	Minimum frequency at which all atoms are excited.
α	Normal vibration spectra of all polymer molecules.
F	Helmoltz free energy.
θ	Debye's temperature.
ν	Number of crosslinked segments, mols.

SUBSCRIPTS

g	Refers to glassy state.
c	Refers to crosslinking.
gc	Refers to a crosslinked polymer in the glassy state.

This study was supported in part by a research grant from the Programa Universitario de Investigación en Salud, UNAM.

REFERENCES

1. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 455 (1943).
2. H. Mark and A. V. Tobolsky, *Physical Chemistry of High Polymer Systems*, 2nd ed., Wiley-Interscience, New York, 1950.

3. A. V. Galanti and L. H. Sperling, *Polym. Eng. Sci.*, **10**, 177 (1970).
4. B. A. Rozenberg, "Epoxy Resins and Composites II" in *Advances in Polymer Science*, Vol. 75, Springer-Verlag, Berlin, 1986.
5. L. Landau and E. M. Lifshitz, *Física Estadística*, Cap. 5, editorial Reverté, México, 1969.
6. S. Z. D. Cheng, *J. Appl. Polym. Sci.*, Applied Polymer Symposia **43**, 315 (1989).
7. B. Wunderlich, *Thermal Analysis*, The University of Tennessee, Knoxville, Tennessee, 1988.
8. B. Wunderlich, *J. Chem. Phys.*, **37**, 1207 (1962).
9. P. J. Flory, *Principles of Polymer Chemistry*, Chap. XI, Cornell University Press, Ithaca, New York, 1953.
10. F. Hernandez-Sanchez, Proceedings, Latin-American Symposium Of Polymers, Guadalajara, Jal., México, 1990, p. 443.
11. F. Hernandez, to be submitted.
12. W. Meesiri, J. Menczel, U. Guar, and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 719 (1982).
13. R. Vera-Graziano, J. Nuñez-Flores, and F. Rivera-Torres, Proceedings, Latin-American Symposium Of Polymers, Guadalajara, Jalisco, México, 1990, p. 1173.
14. T. C. Kendrick, B. Parbhoo, and J. W. White, in *The Chemistry of Organic Silicon Compounds*, S. Patai and Z. Rapoport, Eds., John Wiley & Sons, New York, 1989, Part 2, p. 1289.
15. *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds., John Wiley & Sons, New York, 1986.
16. L. H. Sperling, *Introduction to Physical Polymer Science*, 2nd Edn., Wiley-Interscience, New York, 1992.

Received March 18, 1994

Accepted August 17, 1994