Experimental evidence for trapped chain entanglements: Their influence on macroscopic behaviour of networks

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The swelling and elastic properties of poly(dimethyl siloxane) networks prepared by end-linking and subsequently swollen in heptane and toluene have been investigated as a function of the volume fraction, v_c, at which networks are generated. Increases in both swelling degree and shear modulus with v_c demonstrate the increase in number of trapped entanglements with v_c. The results may be described by a simple scaling law approach.

INTRODUCTION

The existence of trapped chain entanglements in a crosslinked network and their influence on the physical behaviour are controversial[1-15]. We have reported a study of the swelling behaviour of poly(dimethyl siloxane) (PDMS) networks containing various proportions of trapped chain entanglements[16]. The influence of the amount of trapped entanglements on the mesh-size was characterized by inelastic light scattering.

Here, we report on the elastic properties of these PDMS networks. Shear and uniaxial deformation measurements were used to characterize their elastic behaviour.

A new approach, which postulates a topological analogy between an entangled polymer solution and an equilibrium swollen network, leads to a general scaling law between the elastic modulus G and the equilibrium concentration C_e $[G=f(C_e)]$ in a good solvent of the corresponding linear polymer[17,18]. The validity of this scaling law has been proved in equilibrium swollen model networks, approaching the ideal system, in which the proportion of pendant chains was negligible[18].

This approach also allows better insight into the problem of trapped chain entanglements, which introduce supplementary crosslinks into the system. It follows that the number of elastically effective network chains should increase in direct correlation as the mesh-size decrease. Since the elastic modulus, G, is directly related to the number of elastic chains it should increase with increasing numbers of chain entanglements trapped in the system. However, the scaling law $G=f(C_e)$ should remain unchanged.

The number of chain entanglements depends on the volume fraction v_c at which the network is generated and should increase when v_c increases (at least in networks prepared by end-linking of precursor chains).

Thus the mesh-size of a network can be changed either by end-linking precursor polymer chains of a given length at various concentrations v_c[16], or by crosslinking different precursor polymers with different chain lengths at a given concentration v_c[10].

Here, we shall compare the variation of the elastic modulus of networks swollen to equilibrium as a function of the corresponding swelling equilibrium concentration for series of networks prepared by both methods.

A second aspect of this paper will concern the influence of the swelling-solvent quality on the network. When the solvent power decreases, the degree of equilibrium swelling of the gel has been shown to decrease much more than would be expected from the corresponding variation of the molecular dimensions R_G^3 (ref 20) where R_G is the radius of gryation of the elastic chains of the network. This behaviour has been interpreted by an interspersion effect of the elastic chains[21].

The investigation we shall report here was carried out on networks swollen in toluene, which is a moderately good solvent for PDMS and in heptane, a good solvent for this polymer.

THEORETICAL

Swelling equilibrium

The static and dynamic properties of networks swollen in good diluents have been analysed on the basis of the following model: when a network is placed in the presence of an excess of diluent, it is assumed that the swelling of the elementary chains of the network (chain between two first neighbour crosslinks) is the same as that of an equivalent chain between two entanglements in a semi-dilute solution.

$$\varphi_e \propto N^{-4/5}$$

The equilibrium volume fraction φ_e can be identified with the crossover volume fraction φ^* between the dilute and

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semi-dilute regimes of a solution of macromolecules of the same molecular weight as the strands of the network:

$$\varphi^* \propto Na^3/R_F^3 \tag{1}$$

where a is the length of the statistical segment and R_F is the end-to-end distance of a free chain with N segments in the same solvent:

$$R_F = a\left(\frac{1}{2}-\chi\right)^{1/5} N^{3/5} \tag{2}$$

where χ is the Flory–Huggins interaction parameter[22]. Equation (1) which has been called the c^* theorem can be derived from Flory's mean field theory[22] if the change of swelling is assumed to be affine in the dimensions of the network chains.

However, it has been shown that the mean field theory can be used only because of the cancellation of the effects caused by the two following strong approximations: (i) the correlations between segments are neglected; and (ii) the elastic energy of distortion is overestimated as a consequence of the Gaussian chain approximation[17]. Introduction of corrections to take account of these two effects into Flory's lattice model leads to the following formulation for free energy per site:

$$\frac{F}{k_BT} = u\varphi^{2.25} + \frac{3}{2}f\frac{\varphi}{N}\frac{R^2}{R_F^2} + \mu_0(1-\varphi) \tag{3}$$

where u is an effective interaction coefficient which accounts for virial effects and is related to χ through the following equation†:

$$u = \beta(1/2-\chi)^{3/4} \tag{4}$$

φ is the volume fraction of segments, f is a constant which depends on the functionality of the crosslinks of the gel, μ_0 is the chemical potential of the pure solvent, R is the end-to-end distance of the chain at a volume fraction φ and is related to φ through the following packing condition which expresses the affine character of the deformation:

$$\varphi = \delta\frac{Na^3}{R^3} \tag{5}$$

like f, δ is a constant which depends on the functionality of the crosslinks.

When the gel is swollen in an excess of fluid, the chemical potential of the solvent inside and outside the network is the same. The equilibrium volume fraction φ_e can thus be derived from the equality:

$$-\varphi^2\frac{\partial}{\partial\varphi}\left|\frac{F}{\varphi}\right| = \mu_0 \tag{6}$$

which leads to the following expression:

$$\varphi_e = k\left(\frac{1}{2}-\chi\right)^{-3/5} N^{-4/5} \simeq \varphi^*(N) \tag{7}$$

with $k = (0.8\ \delta^{2/3} f \beta^{-1})^{12/23}$.

By combining equations (1), (2) and (7) we can express the end-to-end distance R_e of the elastic chains at swelling equilibrium in the following way:

$$R_e = R_F(\delta/k)^{1/3} \tag{8}$$

At the present stage it may be of interest to compare the results of this approach with those of Flory–Huggins theory. According to the latter theory and under the hypothesis of affine deformation, the variation of φ_e versus N can be approximated in the following way:

$$\varphi_e \propto \left(\frac{1}{2}-\chi\right)^{-3/5} \varphi_0{}^{2/5} N^{-3/5} \tag{9}$$

where φ_0 is the so-called memory term which represents the polymer volume fraction of the swollen network in the reference state[23,24].

This reference state is still the subject of controversy. Many authors have thought that φ_0 could be identified with v_c, the volume concentration at which the network was generated[23–25]. If this is true φ_e should not only be subject to the possible influence of trapped chain entanglements but it should also explicitly depend on v_c according to the equation:

$$\varphi_e \propto \left(\frac{1}{2}-\chi\right)^{-3/5} v_c^{2/5} N^{-3/5} \tag{10}$$

However, there is no clear experimental evidence to confirm the hypothesis $\varphi_0 \sim v_c$.

Alternatively, if we assume that the reference state corresponds to a state in which the chains are Gaussian and unperturbed and that the packing condition (5) is valid, φ_0 is related to N by the following expression:

$$\varphi_0 = \frac{N a^3}{N^{3/2} a^3} \propto N^{-1/2} \tag{11}$$

By combining equations (9) and (11) we obtain the c^* theorem expressed in the relationship (7). In this case φ_e depends only on N for a given polymer–solvent system.

The role played by trapped chain entanglements is also controversial[26–28]. The interpretation given in the present work is based on the hypothesis that in a network swollen in a good solvent the trapped chain entanglements act in the same way as permanent chemical crosslinks. In this case the term N in equation (7) becomes $N_{\text{effective}}$, i.e. the number of statistical segments between two neighbouring crosslinks regardless of whether these are

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† The relation between u and χ can be derived directly from crossover properties. The osmotic pressure of a semi-dilute solution is given by[17]:

$$\frac{\Pi}{k_BT} = 1.25\ \mathrm{u}\ \varphi^{2.25} \sim \xi^{-3}$$

The screening length ξ is related to the end-to-end distance, R_F, in dilute solution through the relationship[17]:

$$\xi^{-1} = R_F^{-1}\left(\frac{\varphi}{\varphi^*}\right)^{3/4}$$

By combining the two above equations with (1) and (2) we obtain:

$$u\left(\frac{1}{2}-\chi\right)^{-3/4} = \text{constant} = \beta$$

Table 1 Variations of the equilibrium volume fractions $\Phi_{e_{\text{hept}}}$ and $\Phi_{e_{\text{tol}}}$ of the PDMS networks swollen in heptane and in toluene, respectively, as a function of the initial volume fraction v_c

v_c	$\Phi_{e_{\text{hept}}}$	$\Phi_{e_{\text{tol}}}$	$\Phi_{e_{\text{hept}}}/\Phi_{e_{\text{tol}}}$
1.00	0.157	0.206	0.76
0.884	0.139	0.182	0.76
0.823	0.139	0.182	0.76
0.772	0.135	0.178	0.76
0.721	0.123	0.164	0.75
0.664	0.121	0.159	0.76
0.559	0.101	0.135	0.75
0.458	0.088	0.119	0.74

trapped entanglements or chemical crosslinks. This point has been confirmed by inelastic light scattering experiments[18].

Elastic modulus

The free energy per site for a gel under uniaxial compressional stress τ can be written[29]:

$$\frac{F}{k_BT}=u\varphi^{2.25}+\frac{1}{2}f\frac{\varphi}{N}\frac{R^2}{R_F^2}\left(\lambda^2+\frac{2}{\lambda}\right)+\frac{\tau a^3}{kT}(\lambda-1)+\mu_0(1-\varphi) \tag{12}$$

where it is assumed that the deformation $(1-\lambda)$ is small $(1-\lambda \ll 1)$ and the volume is constant; k_B is the Boltzmann constant.

The stress–strain relationship can be derived from the following conditions:

$$\frac{\partial F}{\partial \lambda}=0\ ;\ \mu_s=\mu_0 \tag{13}$$

which leads to:

$$\tau=G(\lambda^{-2}-\lambda) \tag{14}$$

where

$$G=\frac{4}{5}\frac{k_BT}{a^3}\beta\left(\frac{1}{2}-\chi\right)^{3/4}\varphi_e^{9/4} \tag{15}$$

or in terms of the number of elastic chains per unit volume of swollen gel, v_0:

$$G=\frac{4}{5}k_BT\,\beta\,k^{5/4}\,v_0 \tag{16}$$

Equations (15) and (16) express the scaling of the shear modulus with concentration, which has already been demonstrated[18].

In the case where a shear stress σ is applied to the gel sample, similar reasoning would lead to:

$$\sigma=G(\lambda-1/\lambda) \tag{17}$$

in place of equation (14).

EXPERIMENTAL

Preparation of poly(dimethyl siloxane) (PDMS) networks

Our PDMS networks were prepared by endlinking α–ω functional precursor chains. Their synthesis, which is based on the classical addition reaction of a hydrogenosilane group onto a vinyl or allyl double bond, has already been described elsewhere[19]. The precursor polymer with endstanding hydrogenosilane functions had a molecular weight $M_n \sim 9700$ daltons. Commercial tetraallyloxyethane, used as a tetrafunctional crosslinker, was treated first with sodium and then distilled from over sodium wire under vacuum. The networks used for the present investigation were prepared in toluene at 75°C in a concentration range between 50 and 100%.

Equilibrium swelling measurements

Equilibrium swelling degrees of the gels were determined according to a weighing technique described earlier[30].

Elastic modulus

Elastic moduli were obtained from unidirectional compression measurements. The apparatus used is similar to that described in the literature[31]. Under compression the dimensions of the samples (cylinders or cubes) could be measured using a profile projector (magnification 10).

In addition we have determined the shear modulus of cylindrically shaped gels (height ~8 cm, diameter ~2 cm) by means of a torsional pendulum method. The period of oscillation of the gel was recorded by an optical method.

RESULTS AND DISCUSSION

Swelling equilibrium

Table 1 shows values of the equilibrium volume concentration φ_e in toluene and in heptane obtained from swelling measurements on tetrafunctional PDMS networks and the volume concentration v_c at which these networks were prepared. The molecular weight of the precursor polymer was $M_n \sim 9700$ daltons. φ_e increases with increasing values of the volume concentration v_c.

Figure 1 shows plots of $\log\varphi_e$ as a function of $\log v_c$. It can be seen that the functions $\varphi_e = f(v_c)$ obey the following power laws rather well:

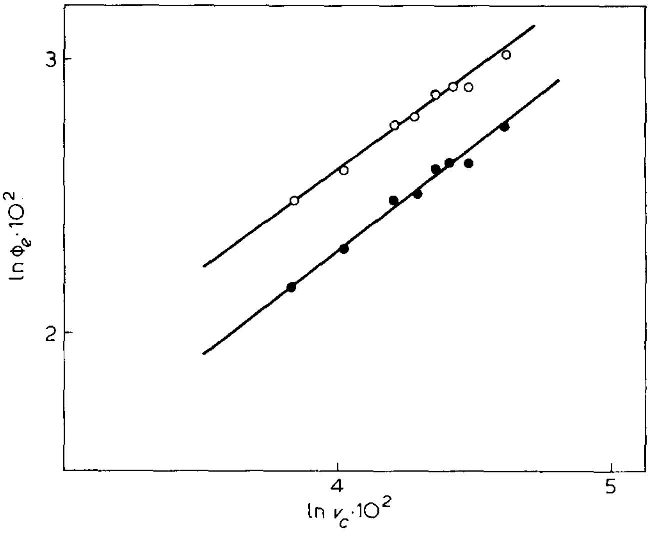

Figure 1 Variation of the swelling equilibrium volume fraction of PDMS networks as a function of the initial volume fraction. ○, Toluene; ●, heptane. Straight lines represent the best least square fits and have slopes equal to 0.71 for toluene and 0.75 for heptane

$$\varphi_e \sim v_c^{0.75} \quad \text{for PDMS networks swollen in heptane} \tag{18}$$
$$\varphi_e \sim v_c^{0.71} \quad \text{for PDMS networks swollen in toluene}$$

None of the proposed theoretical approaches can explain the experimentally observed behaviour if chain entanglements are not considered. Equation (7) predicts that φ_e is independent of v_c whereas φ_e should vary as $v_c^{0.4}$ if we take into account a memory effect (equation 9). This discrepancy cannot be attributed to the presence of pendant chains, since their number should not vary much in the concentration range considered[16]. In addition, pendant chains have practically no influence on degree of equilibrium swelling[32].

If we assume now that the number of trapped entanglements increases with v_c and that they act as additional crosslinks, then the average value of N decreases and φ_e increases in correlation.

Thus a well-defined relationship may exist between the mesh size of a network swollen at equilibrium in a good diluent and that of the transient network formed by the corresponding semi-dilute solution of the polymer precursor prior to crosslinking. This is supported by the following reasoning.

According to the c^* theorem, the number of statistical segments N between two neighbouring crosslinks of a swollen network is related to the equilibrium volume fraction φ_e by:

$$N \sim \varphi_e^{-5/4} \tag{19}$$

Combining (18) and (19):

$$N \sim v_c^{-0.94} \text{ in heptane;} \quad N \sim v_c^{-0.89} \text{ in toluene} \tag{20}$$

Alternatively, at the concentrations used in the preparation of the networks ($0.5 < v_c < 1$), the precursor solutions can be considered as theta solutions. In this case, the mean field theory predicts the following law for the number of statistical segments N_i associated with the mesh size of the transient network[33]:

$$N_i \sim v_c^{-1} \tag{21}$$

Comparison of equations (20) and (21) shows that N is nearly proportional to N_i.

However, this interesting result, establishing a close correlation between the mesh size of the networks at swelling equilibrium and that of the entanglement networks in the solution of polymer precursor could be coincidental and deserves further investigation.

We have also calculated the ratio of the equilibrium volume concentrations in both solvents: $\varphi_{e_{\text{Hept}}}/\varphi_{e_{\text{Tol}}}$, According to equation (7):

$$\varphi_{e_{\text{hept}}}/\varphi_{e_{\text{tol}}} = \frac{u_{\text{hept}}^{-4/5}}{u_{\text{tol}}^{-4/5}} \tag{22}$$

should be a constant, and this is observed experimentally (*Table 1*).

Elastic Modulus

Stress–strain measurements. The stress–strain relation (14) has been established assuming that the volume of the gel sample remains constant under compression. Because of the large size of the samples (5 cm^3) and the low value of the diffusion constant of the gel[34] the deswelling arising from the compression requires a long time (typically a few hours). As a consequence, the incompressibility assumption is fulfilled if the measurements are performed within about 15 min of the application of the compressional stress. Moreover, our experimental set-up allowed us to measure both the height and the section of the deformed samples.

If f_z is the force applied along the z axis on a section of initial area A_i, the stress τ is given by equation (14):

$$\tau = f_z/A_i = G(\lambda^{-2} - \lambda) \tag{23}$$

We can also define the stress τ' with respect to the area A_d of the deformed gel:

$$\tau' = f_z/A_d = G(\lambda^{-1} - \lambda^2) \tag{24}$$

For an incompressible gel both $\tau = f(\lambda^{-2} - \lambda)$ and $\tau' = f(\lambda^{-1} - \lambda^2)$ should fit a single straight line with a slope equal to the shear modulus G. This is indeed what is observed (*Figure 2* In *Figure 3* are reported the variations of the radial deformation $\varepsilon'_D = \ln(D_d/D_i)$ of a cylindrical sample as a function of the axial deformation $\varepsilon'_L = \ln(L_d/L_i)$ where D and L are the diameter and the length of the cylinder, the subscripts i and d referring to initial and deformed, respectively. The Poisson coefficient, given by the slope of the straight line obtained is found to be 0.52, in close agreement with the theoretical value 0.5 for incompressible materials.

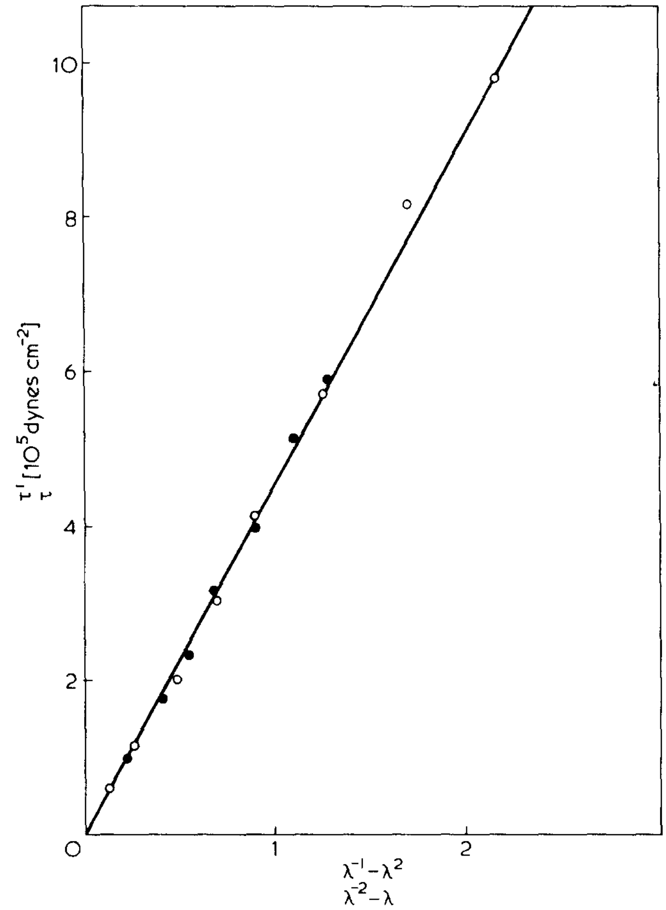

Figure 2 Variation of $\tau = f(\lambda^{-2} - \lambda)$ and $\tau' = f(\lambda^{-1} - \lambda^2)$ for a PDMS network swollen in toluene ($v_c = 0.72$). τ and τ' refer to the stress per unit area for the undeformed and the deformed sample, respectively

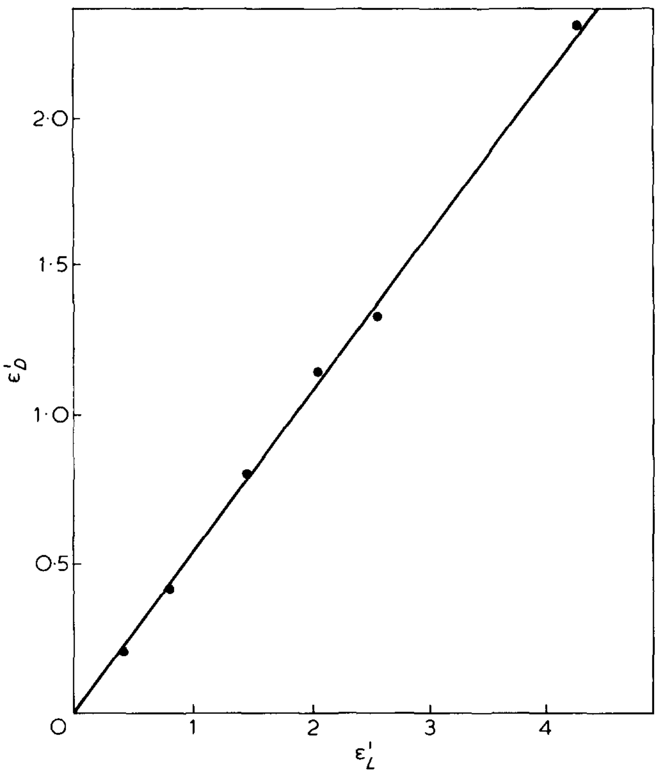

Figure 3 Radial *versus* axial deformation for a PDMS network swollen in toluene (v_c = 0.72)

A further check on the validity of the measurements of shear modulus is provided by comparison of values of G determined from compressional experiments and those obtained from the torsional pendulum method. *Table 2* shows the results for two samples. These results, as well as several others not reported here, show that the agreement is satisfactory.

Influence of the trapped entanglements on the shear modulus. In earlier studies, it was commonly assumed[24] that the influence of concentration at gel formation, v_c, on the elastic modulus was due to a memory effect of the dimensions of the elastic chain.

According to classical theory, the elastic modulus is defined by

$$G = ARTv_e\varphi_0^{2/3}\varphi_e^{1/3}$$

where v_e is the number of network chains per unit volume of dry gel. Assuming as before ${\varphi_o}^{2/3} \sim {v_c}^{2/3}$,

$$G{\varphi_e}^{-1/3} = ARTv_e v_c^{2/3} \qquad (25)$$

Figure 4 is a plot of $G{\varphi_e}^{-1/3}$ *versus* v_c on a double logarithmic scale for a series of samples swollen in toluene. The experimental points lay on a straight line with slope 1.58.

Thus, a memory-effect cannot explain the observed behaviour, and a predominant influence of trapped chain entanglements must be involved.

Figure 5 is a double logarithmic plot of the shear modulus of PDMS networks swollen in toluene as a

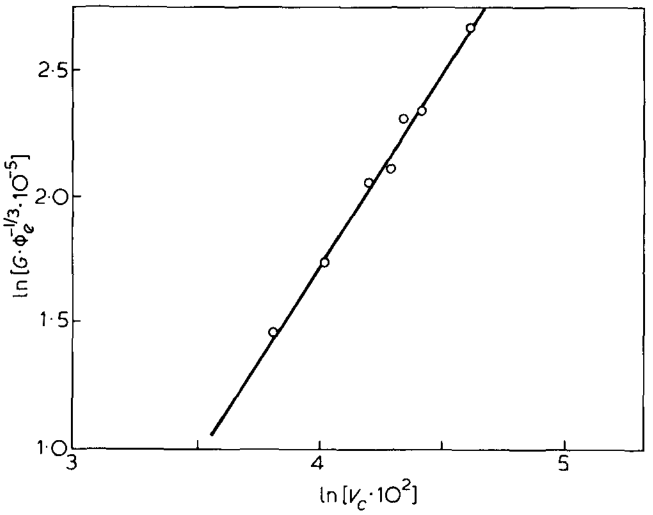

Figure 4 Variation of $G\ \Phi_e^{-1/3}$ as a function of ν_c for PDMS networks swollen in toluene. Straight line is the best least square fit

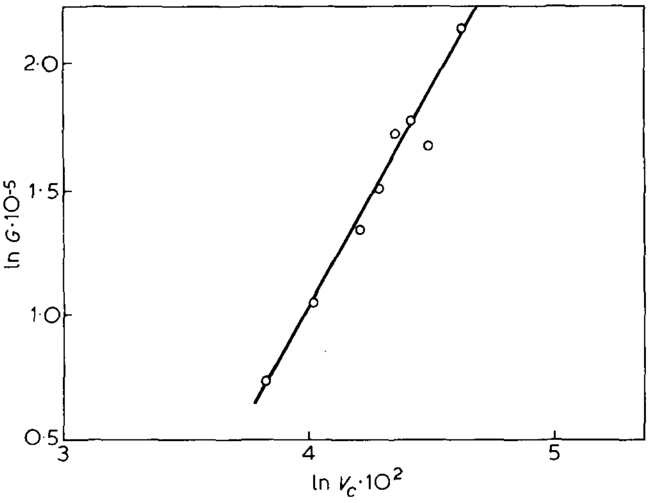

Figure 5 Shear modulus as a function of the initial volume fraction for PDMS networks swollen in toluene. The strong deviation observed for one point seems accidental. This point has not been taken into account for the calculation of the least square fit which is represented by a straight line of slope 1.8

Table 2 Shear moduli of PDMS networks swollen in heptane and toluene, respectively. G^S refers to measurements performed by the torsional pendulum method

ν_c	G_{hept} (10^5 x dynes. cm^{-2})	$\Phi_{e_{\mathrm{hept}}}$	G_{tol} (10^5 x dynes. cm^{-2})	G^S_{tol} (10^5 x dynes. cm^{-2})	$\Phi_{e_{\mathrm{tol}}}$
1.00	7.6	0.157	8.5		0.206
0.884	4.4	0.139	5.3	4.9	0.182
0.823	5.4	0.139	5.9		0.182
0.772	5.3	0.135	5.7		0.178
0.721		0.123	4.5		0.164
0.664		0.121	4.2	4.2	0.159
0.559	2.5	0.101	2.9		0.135
0.458	1.9	0.088	2.1		0.119

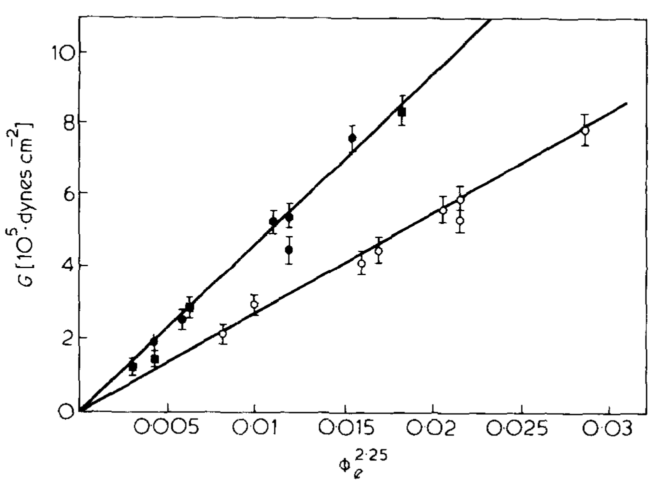

Figure 6 Variation of G as a function of $\Phi_e^{2.25}$ for PDMS networks swollen in heptane (●) and in toluene (○). ●, Networks prepared at different initial concentrations; ■, networks prepared from polymer precursors of different molecular weight ($v_c = 0.67$). Straight lines are the best least square fits (the origin has been taken as an experimental point)

Table 3 Shear moduli of PDMS networks prepared from precursor polymers of different molecular weight and swollen to equilibrium in heptane

M_n	G (10^5 x dynes cm^{-2})	Φ_e
4500	8.33	0.169
8700	2.68	0.104
13500	1.38	0.089
17100	1.14	0.076

function of the polymer volume fraction v_c. Data fit reasonably well with the power law:

$$G \sim v_c^{1.8} \quad \text{(toluene).}$$

Networks swollen in heptane give a similar law:

$$G \sim v_c^{1.9} \quad \text{(heptane)}$$

This result supports the hypothesis of the existence of a correlation between the topology of the entangled solution prior to crosslinking and that of the final network. It was shown in the theoretical section that the shear modulus of a network swollen at equilibrium should scale with N according to:

$$G \sim \varphi_e^{9/4} \sim N^{-9/5}$$

If we trust the result of the preceding paragraph, i.e. $N \sim N_i \sim v_c^{-1}$ we find:

$$G \sim v_c^{-1.8}$$

which is a power law very close to the experimental.

In *Figure 6* we have reported the variation of the shear modulus *versus* $\varphi_e^{9/4}$ for the series of PDMS networks swollen in heptane. On the same graph are plotted data obtained from earlier measurements on PDMS networks prepared at a given concentration ($v_c = 0.67$) from polymer precursors of different molecular weights (see *Tables 2* and *3*).

For each solvent both sets of data lie on the same straight line which passes through the origin, within the accuracy of the experimental points. This shows unambiguously that for a network swollen in a good diluent, the trapped entanglements play exactly the same role as the chemical crosslinks. Furthermore, the φ_e dependence of G is well-described by a power law with an exponent close to the theoretical 9/4.

Influence of the quality of the diluent. Comparison between the shear behaviour of PDMS networks swollen in heptane and toluene respectively is also illustrated in *Figure 6*. The same scaling law is obtained for both diluents.

For affine deformation, it is expected that the slope of the straight line $G = f(\varphi_e^{2.25})$ decreases with decreasing solvent power (equation 15). This is observed experimentally. However, the best test to characterize the deformation process is provided by the variation of $(G/\varphi_{e\text{Hept}})$ as a function of $(G/\varphi_{e\text{Tol}})$. In an affine deformation process (G/φ_e) is a function of the molecular weight of the elastic network chains only (equation 16 and Ref. 17). As a consequence, $G/\varphi_{e\text{Hept}}$ should be a linear function of $(G/\varphi_{e\text{Tol}})$ with a slope equal to 1.

The experimental data reported in *Figure 7* fit a straight line with slope 1.2. This behaviour suggests a slightly non affine deformation of the network when heptane is replaced by toluene as a swelling solvent. Recent neutron scattering experiments have shown that the deviation from affineness becomes more and more pronounced as the solvent power decreases and as the molecular weight of the polymer precursor increases[20,35].

This effect has been qualitatively attributed to a chain interspersion process in which the average distance between two spatially neighbouring crosslinks decreases more than that of two topological neighbours[21,36].

CONCLUSION

We have investigated the degree of swelling equilibrium and the shear modulus of PDMS networks prepared by

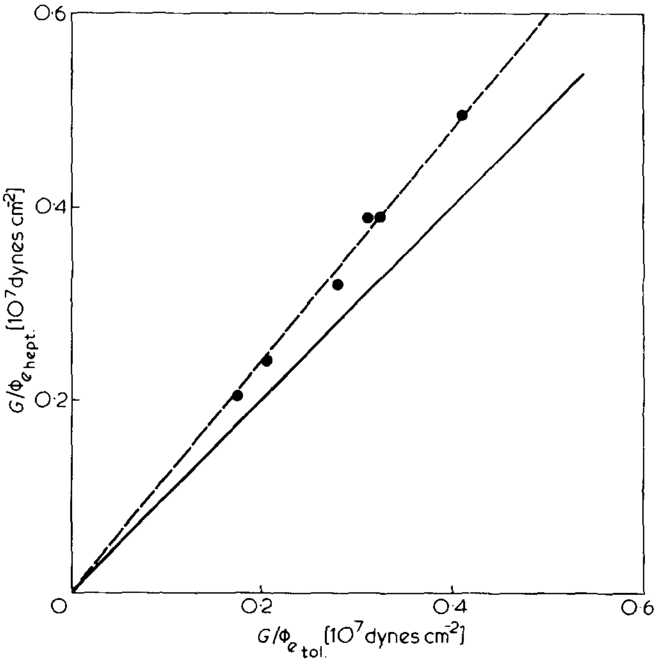

Figure 7 Variation of $(G/\Phi_{e_{\text{hept}}})$ *versus* $(G/\Phi_{e_{\text{tol}}})$ for PDMS networks. The full line has a slope of 1. The broken line is the least square fit to the data. Origin has been taken as an experimental point

end-linking at volume fractions v_c ranging from 50% up to bulk. The results demonstrate the presence of an increasing number of trapped entanglements when v_c increases. Of particular interest is the fact that the elastic moduli of networks swollen in heptane vary with the equilibrium volume fraction φ_e of the gels according to the same scaling law, $G \sim \varphi_e^{2.25}$, for both the series prepared at variable v_c and a series prepared at given v_c but in which the mesh size was changed using precursor polymers with different molecular weights. These results strongly support the model in which the trapped chain entanglements act as supplementary crosslinks in the swollen network and are responsible for a decrease of the mesh size of the system. This mesh size, which is given by the average distance between two neighbouring junctions regardless of whether these are trapped entanglements or chemical crosslinks, is the only parameter which controls the elastic and swelling properties of a network in a good diluent.

The results obtained for PDMS networks swollen in toluene (which is a poorer solvent than heptane) demonstrate a slightly non-affine deformation of the gel on decreasing the quality of the diluent. Thus previous results on gels of different chemical nature[20,21] are confirmed.

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