Dependence of properties of swollen and dry polymer networks on the conditions of their formation in solution

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(Received 5 November 1984)

A marked difference between the properties of networks first crosslinked and then swollen, and those synthesized in a solvent medium, has been shown. The present investigation was carried out using two different types of regular networks, polysiloxane and polyisocyanurate networks, which had different chain flexibilities, crosslinking densities, and intermolecular interactions. The concentration at which the network is formed v_0 and the quality of the solvent were varied over a wide range. It was found that with a decrease of v_0 from 1–0.05, the elastic modulus of both gels and dry networks obtained from these gels after removing the solvent decreased by a factor of 2–4 and equilibrium swelling decreased a few times.

(Keywords: networks; gels; poly(dimethyl siloxane); polyisocyanurate; viscoelastic properties; swelling)

INTRODUCTION

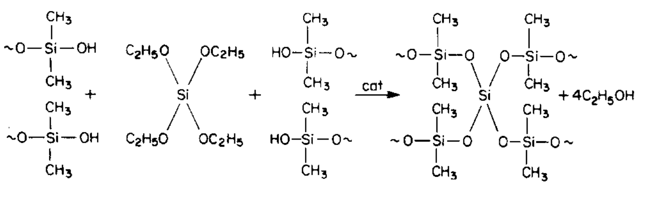
The difference between network polymers, formed in the absence of a solvent, from those formed in a swollen state, in a solvent medium is due to differences in the reference state as well as to the differences in their structure.

The dependence of the properties of crosslinked polymers on the concentration C_0 at which the network is formed in solution was studied by a number of researchers[1-6]. In recent years this difference has been clarified by the use of model networks of regular structure obtained in the form of gels[7-10]. However, in most of these works the concentration was varied within a rather narrow range.

The purpose of the work presented here was to establish the possible range of variations of the rheological and thermodynamical properties of the gels formed during the synthesis of network polymers. These variations are provided by changing the concentration v_0 of the networks formed in solution over a very wide range and by changing the nature of the solvent.

Two types of regular chemical networks, namely crosslinked poly(dimethyl siloxanes) and polyisocyanurates, differing in chain flexibility, intermolecular interaction and crosslinking density, were selected. The poly(dimethyl siloxane) (PDMS) gels were prepared by the 'in solution' 'cold vulcanization' of α,ω-dihydroxyoligo and poly(dimethyl siloxanes)s with tetraethoxysilane in the presence of tin diethyl-dicaprylate (see *Scheme 1*)[11-13]. As can be seen the reaction proceeds at the end hydroxyl groups of the polymers.

Scheme 1



In such networks, the molecular mass of crosslinked oligomers and polymers determines the distance between crosslinks M_c.

The characteristics of the original oligomeric and polymeric PDMS are shown in *Table 1*. Toluene (polymer–solvent interaction parameter $\chi = 0.445$), siloxane liquid ($\chi = 0.484$), heptane ($\chi = 0.409$), ethyl acetate ($\chi = 0.5$) and a mixture of toluene and acetonitrile (nonsolvent) in various ratios were used as solvents. The volume fraction of the polymer in solution V_0 was varied within the range of 0.05–1, and the molar ratio of the cross-linking agent to the polymer was varied from 0.25 to 16.

Polyisocyanurate gels (PIC gels) were obtained by the polycyclotrimerization of diisocyanate in solution[14] according to *Scheme 2*. The volume fraction v_0 varied from 0.05 to 1 (ref. 15). 4,4-Diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HMDI) and macrodiisocyanate obtained in the reaction of 2,4-toluylene diisocyanate with oligo(propylene glycol) ($M_n = 1052$) were used. Nitrobenzene, anisole and *N*-methylpyrrolidone were used as solvents. The quality of the solvents was defined with respect to equilibrium swelling of gels.

Scheme 2

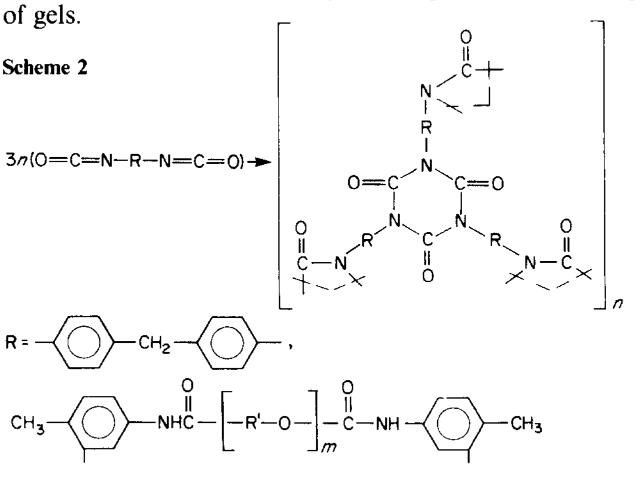


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Table 1 Characteristics of siloxane oligomers and polymers cross-linked at the terminal OH-groups

No.	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_v$	ρ (kg/m^3)	T_g (°C)
1	970	–	–	976	–130
2	2080	2.40	5000	–	–118
3	5050	–	–	–	–
4	6050	2.90	17 550	–	–
5	11000	2.70	29 700	975	–110
6	26000	1.46	37 960	973	–
7	65000	1.35	87 750	971	–110

The shear modulus of the original gels G_i was obtained, and then the gels were washed in a good solvent for 80 h using a Soxhlet apparatus. The equilibrium swelling degree Q (or its reciprocal value, the volume fraction of the polymer in a swollen sample V_2) of the gel in this solvent as well as the shear modulus G_e of the gel swollen to equilibrium were measured, and then the gels were dried slowly (in order to prevent large internal stresses and cracking of the samples) and the shear modulus of 'dry' networks G_d was measured; these 'dry' networks were subjected to repeated equilibrium swelling and their G'_e and V'_2 were measured. The data obtained were used for calculating the structural parameters of the network, in the first place the number of crosslinks and elastically-effective chains of the network (according to statistical theories of rubber-like elasticity and swelling):

$$M_c = \frac{\rho}{v_e} = \frac{ARTv_2^{1/3}v_0^{2/3}\rho}{G} \tag{1}$$

$$M_c = \frac{\rho}{v_e} = \frac{\bar{V}_i\rho[(2/f)v_2 - Av_2^{1/3}v_0^{2/3}]}{\ln(1-v_2)+v_2+\chi v_2^2} \tag{2}$$

where v_e is the number of elastically-effective chains in moles per unit dry polymer volume, ρ is the dry network density, $\bar{V}_i$ is the molar volume of the solvent, A is the front-factor, R is the universal gas constant, T is the temperature, f is the functionality of the network.

The equilibrium swelling degree was evaluated by the weight method, the drops of the solvent being removed from the sample surface with filter paper.

The shear modulus of the gels was evaluated by the methods of uniaxial compression and penetration with a spherical indentor following the equation[16]:

$$G = \frac{3F}{16R^{1/2}h^{3/2}} \tag{3}$$

(where R is the radius of the indentor, h is the depth of penetration, F is the force) as well as in shear experiments in a specially designed rotation viscosimeter of constant stresses[17].

To calculate the viscosities (η) over a wide range of values beginning with very small ones ($\eta = 0.1$ Pa·s) as well as to use a possibility of applying small stresses τ ($\tau > 2$ Pa) the viscosimeter was supplied with changeable working cylinder blocks having large surfaces.

As is seen in *Figure 1a* and *1b*, in the case of siloxane gels which had been crosslinked in the viscometer at constant stress it was possible to fix with sufficient precision the gel-point (t_g) as well as to evaluate the viscosity which increased up to the gel-point[13] and the shear modulus, which increased after the gel-point had reached its equilibrium value. The possibility of measuring these parameters in the vicinity of the gel-point, which usually is difficult, makes it possible to specify scale laws,

$$\log \eta - \log \frac{\alpha_g - \alpha}{\alpha_g} \quad \text{and} \quad \log G - \log \frac{\alpha - \alpha_g}{\alpha_g}$$

(where α is the conversion), *Figure 2*, and to define the value of the critical exponent (considering that conversion is proportional to the time t and $G \approx (t - t_g)/t_g)^{18}$. For siloxane obtained both in solution and in the absence of solvent, this exponent was equal to ≈ 1 in the range of $\Delta t < 10$ min, which is markedly less than 1.7–1.8 predicted by the theory[19]. This dependence undergoes considerable changes away from the gel-point.

Dependence of gel properties on the concentration of the solution in which the network is formed

Tables 2 and *3* represent the results of all the measurements. Analysis of these data has shown that the networks formed in solution have considerably lower shear moduli and a much larger extent of equilibrium swelling (smaller value of V_2) when compared with the swollen networks

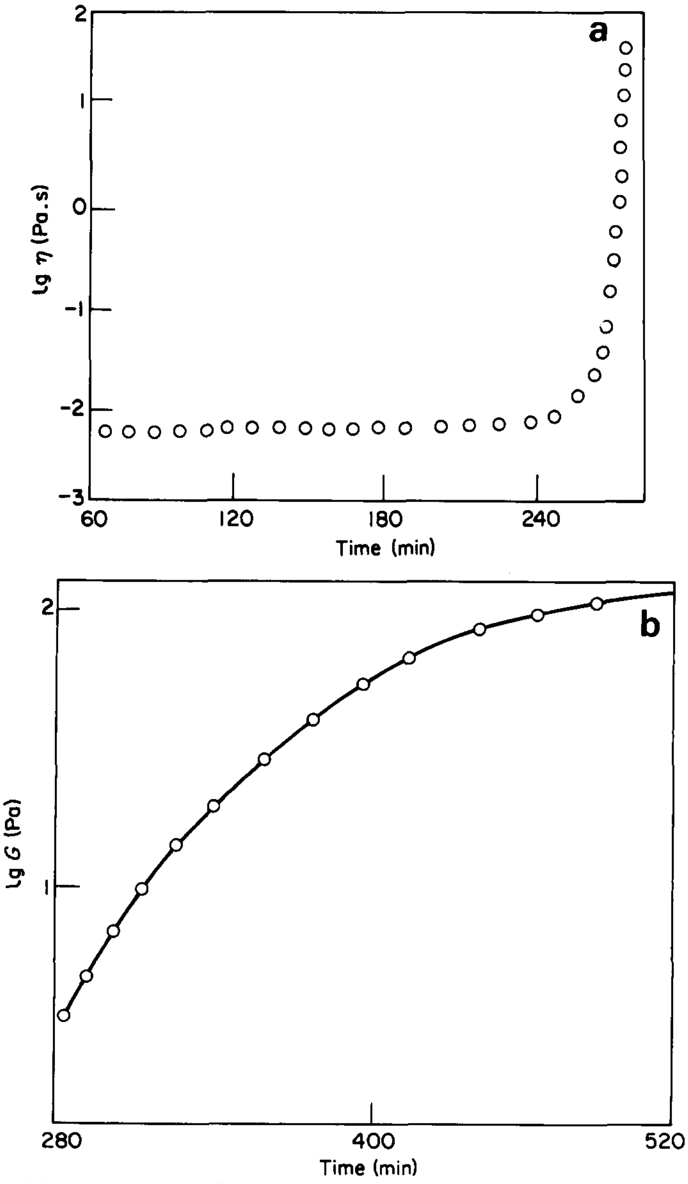

Figure 1 Kinetics of viscosity (a) and shear modulus (b) growth in the gelation process of 10% gel of α,ω-dihydroxyoligodimethyl siloxane ($\bar{M}_n = 11\,000$) in heptane

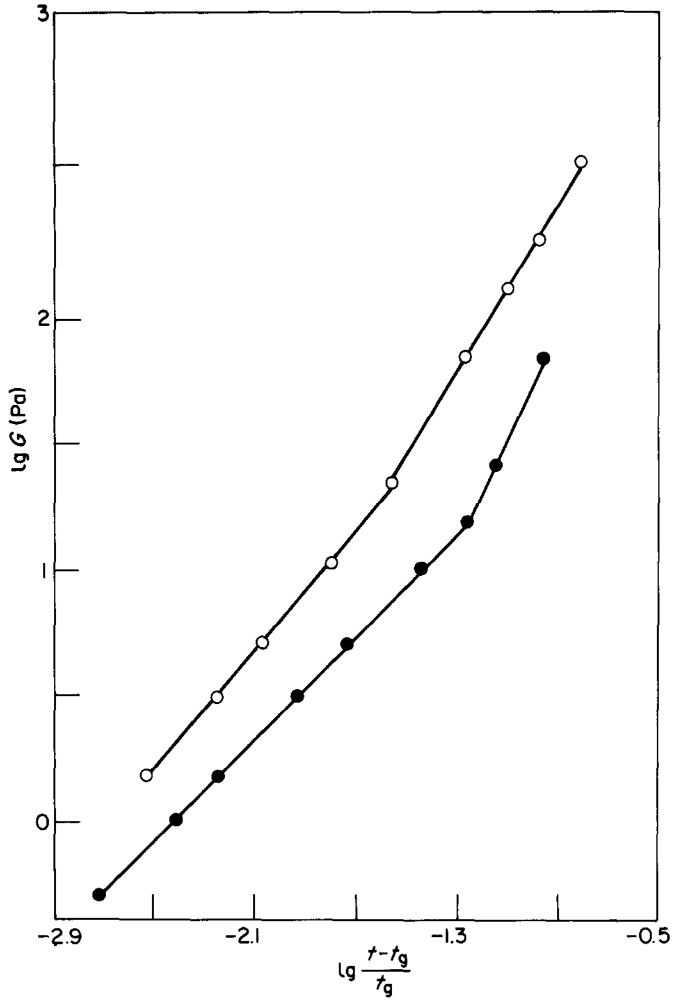

Figure 2 Growth of shear modulus in time in the vicinity of the gel-point in scaling coordinates

obtained in the absence of the solvent ($v_0 = 1$). This phenomenon is exhibited more markedly at higher dilutions. With a decrease of the concentration C_0 from 100 to 5% the shear modulus of elastomeric siloxane networks decreases by the order of 2 while that of glasslike polyisocyanurate networks decreases by the order of 4. Hence, the influence of the solvent increases with the greater intermolecular interaction and crosslinking density. These variations exceed those corresponding to viscoelastic theories when, according to equation (1), the shear modulus of the gel decreases proportionally to $v_2^{1/3}$, or, taking account of modified theories[1], decreases to some greater degree by ($v_2^{4/3}$). The variations are markedly greater than the variations of the modulus due to a change of $\bar{M}_n$ of the crosslinked oligomer, or, in other words, the crosslinking density.

Such a wide range of variations of the shear modulus may result only from a considerable difference between the structure of the network obtained in solution and that obtained in the dry state.

The data on the equilibrium swelling lead to the same conclusion. Thus in case of the siloxane network obtained in the absence of the solvent, the concentration v_2 of the polymer in the gel, swollen in heptane to equilibrium, is equal to 0.208; the network obtained in the same solvent at the same concentration does not retain the given equilibrium amount of the solvent and additionally swells to $v_2 = 0.067$. Formation of the networks at a considerably lower concentration does not result in syneresis of the excess of solvent, that is, the gels formed appear to be one phase in the whole range of concentrations and are always capable of still greater equilibrium swelling.

The molecular mass of the crosslinked oligomer determines the lowest concentration of the polymer in solution v_0^{lim} at which the formation of the network is possible: the smaller is $\bar{M}_n$ of the oligomer, that is, the greater is the crosslinking density, the greater is v_0^{lim}. Thus, for example, at $\bar{M}_n = 1100$, v_0^{lim} is equal to 2%, at $\bar{M}_n = 970$, v_0^{lim} is 10%.

It is well known that for two-phase gels, e.g. poly(hydroxyethyl methacrylate), the equilibrium swelling does not depend on the concentration of the network formation, while the excess of the solvent (introduced upon synthesis) synerizes[20,21]. The results obtained in the present work lead to the conclusion that, by contrast, the one-phase chemical network at a given composition, generally speaking, does not have any definite equilibrium swelling since it is determined in every particular case by the pre-history of the network formation in solution.

The same holds for poly(isocyanurate) networks, although they are not capable of additional swelling. This is probably due to the impossibility of conformational changes in the rather rigid chains of the highly crosslinked network.

Table 3, however, shows that for these gels $v_2 = v_0$; at equilibrium they retain that amount of the solvent which is given during synthesis. The gels of higher rubber-like elasticity are formed in this case at high dilutions (5–10%) instead of rigid glass-like polymer. Since the polyisocyanurate network obtained without a solvent is never capable of swelling, it is obvious that for highly crosslinked networks a change in the concentration at which

Table 2 Properties of siloxane gels in heptane and dry networks obtained from them and their dependence on molecular mass of oligomers being crosslinked and on concentration of the latter in solution at the network formation

$\bar{M}_n$	v_0	ρ	$G_i \times 10^{-4}$	$G_e \times 10^{-4}$	$G_d \times 10^{-4}$	v_2	v'_2
1	2	3	4	5	6	7	8
970	0.2	1042	–	26.00	56.0	0.240	0.410
	0.5	1015	–	48.00	61.0	0.260	0.39
	1.0	997	–	120.00	215.0	0.420	0.610
2080	0.2	1018	–	7.80	31.0	0.180	0.260
	0.5	1005	–	39.00	60.0	0.361	0.397
	1.0	996	–	68.00	100.0	0.401	0.416
5050	0.1	1003	–	0.47	13.1	0.056	0.251
	0.2	1000	–	3.10	14.2	0.114	0.217
	1.0	995	–	39.0	58.0	0.297	0.343
6050	0.2	983	–	1.80	6.9	0.090	0.113
	1.0	997	–	29.0	52.0	0.240	0.277
11 000	0.05	1017	0.15	0.12	9.1	0.041	0.262
	0.1	989	0.85	0.70	4.5	0.055	0.078
	0.2	982	5.61	0.80	10.0	0.069	0.094
	0.5	978	16.00	6.30	22.0	0.126	0.261
	1.0	975	34.00	16.00	40.0	0.208	0.246
26 000	0.05	983	0.11	0.06	6.2	0.022	0.058
	0.1	976	0.45	0.260	2.5	0.044	0.075
	0.2	975	2.90	0.67	5.3	0.059	0.083
	0.5	973	11.00	3.50	16.0	0.123	0.160
	1.0	971	24.00	12.00	31.0	0.172	0.213
65 000	0.05	980	0.08	–	–	–	–
	0.1	974	0.25	0.08	–	0.015	0.051
	0.2	973	0.73	0.28	4.4	0.029	0.065
	0.5	972	7.13	2.80	8.7	0.087	0.140
	1.0	971	19.00	10.40	26.6	0.162	0.206

Table 3 Properties of polyisocyanurate gels and dry networks and their dependence on the nature of the solvent and molecular mass of the original diisocyanate

Diisocyanate/solvent	v_0	v_2	v_2 N-MP	v_2 A	G_e (MPa)	G_d (MPa)	ρ (kg/m^3)
1	2	3	4	5	6	7	8
MDI/*N*-methylpyrrolidone	0.05	0.046	0.137	0.460	0.026	45	1211
	0.10	0.106	0.145	0.333	0.087	50	1213
	0.20	0.203	0.247	0.505	0.640	63	1214
	0.50	0.500	0.505	0.540	2.200	70	1217
	0.70	0.700	–	–	6.300	74	1258
	1.00	1.000	1.000	1.000	–	220	1273
MDI/anisole	0.05	0.050	0.170	0.270	0.022	11	–
	0.10	0.137	0.250	0.300	0.200	25	1127
	0.20	0.233	0.250	0.420	1.050	31	1156
	0.50	0.500	0.490	0.560	8.900	37	1179
Macrodiisocyanate/nitrobenzene	0.20	0.120	0.094	0.100	0.065	0.18	1102
	0.50	0.210	0.302	0.216	0.220	0.73	1103
	1.00	0.260	0.220	0.280	0.370	1.50	1094

they are formed results in specifically wide range of variations in their structure and therefore their properties.

Analysis of the concentration dependence of the shear modulus also proves that there is a significant difference in the structure of the networks formed in various conditions. *Figure 3* shows that for the gels obtained in the absence of the solvent with a constant number of crosslinks, this dependence is expressed as $G \sim v_2^{1/3}$, this being in good agreement with statistical theory of rubber-like elasticity. For the gels formed in solution at various concentrations the exponent of this dependence is 1.7–1.8. For the same gels, though swollen to equilibrium, this exponent is 2.2–2.7. The exponent increases with an increase of the chain rigidity, intermolecular interaction and crosslinking density. The values of these exponents are very close to experimental ones obtained for thermoreversible gels formed by physical crosslinks. They are also close to the theoretical value 2.25 obtained using scaling approaches[19]. The latter are common for the gels obtained in solution due to both chemcal and physical bonds and result from the decrease of the number of bonds in the gel network with a decrease of the concentration at which they are formed.

It is of interest that the gels obtained in solution at a given concentration and subjected to different swelling degrees (in which the number of elastically effective chains remain constant, as is the case with the gels obtained without a solvent) are characterized by another value of the exponent. *Figure 4* shows that its value increases regularly with a decrease of the concentration at which the gel is formed. This means that the theory of rubber-like elasticity is not able to describe the networks formed in solution because of the substantially different topology of these networks.

Therefore, the whole set of the data obtained through the measurements of the shear modulus and swelling ratio of the gels obtained in the course of chemical network formation in solution, is indicative of the decreasing number of elastically effective network chains as a result of the decreasing concentration v_0. It results in the formation of a considerably smaller number of elastically effective chains and, accordingly, crosslinks in the actual networks than the number of the crosslinks defined according to the amount of the crosslinking agent.

Increasing defectiveness of the network structure due to dilution

Changes in network structure during dilution can be caused by several factors involved with the sources of the network defects. Amongst these are: decreases in the

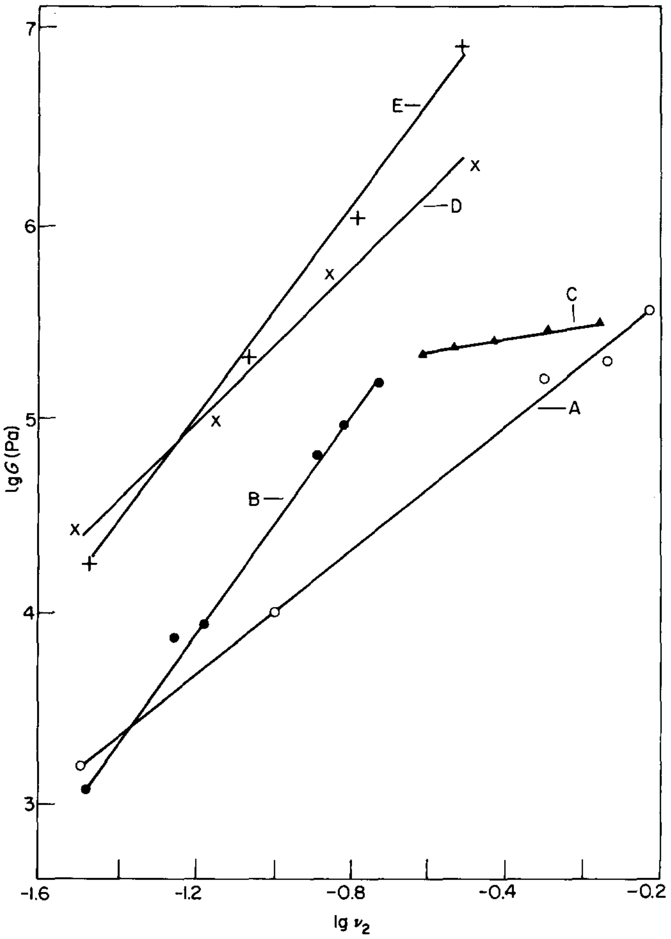

Figure 3 Concentration dependence of the shear modulus of siloxane (Curves A, B and C) and polyisocyanurate (Curves D and E) gels prepared by various methods; (△): the network is prepared at $V_0=1$; (○): the original gels obtained at various v_0; (●): the same gels swollen to equilibrium; (×): polyisocyanurate gels swollen to equilibrium in a good solvent (*N*-methylpyrrolidone); (+): the same gels swollen in nitrobenzene (poor solvent)

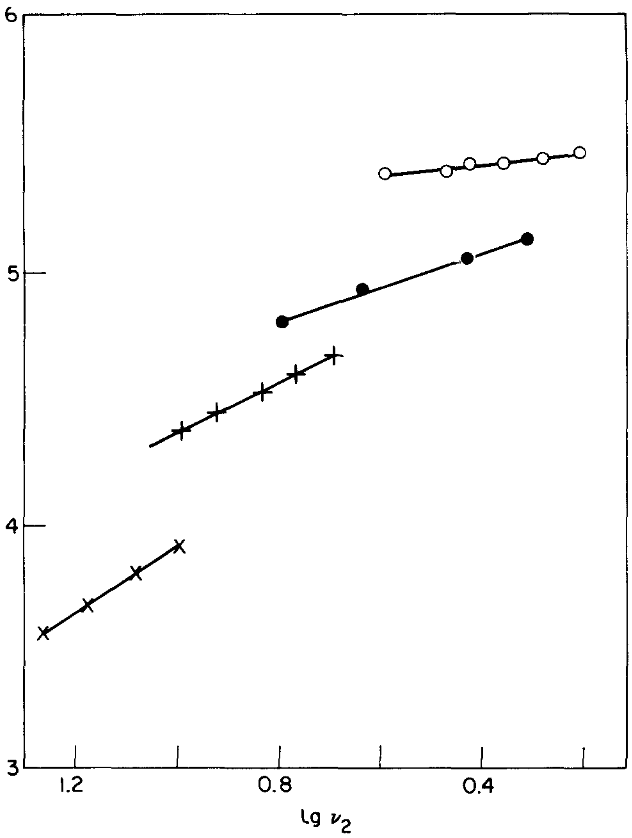

Figure 4 Variation of the shear modulus during the swelling of the gels prepared at the following values of v_0; (○): 1; (●): 0.5; (+): 0.2; (×): 0.1

number of physical crosslinks (entanglements or intermolecular contacts); increases in the intramolecular cyclization[22]; an increase in the number of pendant chains exhibiting only one functionality in the network; and a predominance of the microgelation mechanism.

For polystyrene networks, it has been shown[23] that increasing the number of pendant chains (the number being given according to the conditions of the synthesis in solution) results in a decrease of the elastic modulus but has no effect upon the equilibrium swelling.

However, an increase in the number of unreacted oligomer ends on the introduction of 0.25 moles of the crosslinking agent per mole of oligomer (which is considerably less than the stoichiometric amount) leads to a simultaneous decrease of the shear modulus and an increase in swelling (*Figure 5*).

At present it is impossible to evaluate experimentally the part of intramolecular cyclization in the process of network formation. One of the direct indications of this process and its increasing role on dilution appears to be the complete absence of the gel in the course of polycyclotrimerization of dicyanate in 2% solution in spite of 100% conversion, that is, the formation of a completely soluble crosslinked system[24]. It is this particular tendency to macrocyclization that, also in the case of polycyclotrimerization of diisocyanates, leads to the marked changes in the properties of polyisocyanurates occurring with variations of concentration, v_0, at which they are synthesized in solution.

The considerable part played by intramolecular crosslinking in the process of siloxane network formation in 5% solution is indirectly indicated by the fact that when the solvent is removed from the 5% gel, in the dry network, as it can be seen in *Figure 6*, a distinct globular structure appears (typical also for the networks of another chemical structure synthesized in solution)[25,26]. For the networks obtained in the absence of the solvent, this structure, according to electron-microscopic data, is absent. According to ref. 26, the appearance of the globular structure results from the intramolecular process of crosslinking which then leads to the formation of highly crosslinked beads and particles of the microgel.

The increasing number of defects in the network formed in solution causes rather high rubber-like elasticity and creep of 5% gels of polyisocyanurates in a good solvent, *N*-methylpyrrolidone, as it is seen from *Figure 7*. Thus, when the process of intramolecular cyclization prevails, the high density of the original chemical network does not necessarily become a prerequisite for the brittleness of the gels obtained on this basis. In the cases when these processes do not occur (e.g. in rigid chain polyamides upon high dilution), gels of high brittleness are formed[27].

The viscoelastic properties of siloxane gels are also indicative of the presence of cyclization and its increasing effect with decreasing molecular mass of the crosslinked oligomer. *Figure 8* shows that in the networks obtained without a solvent and at concentrations above 20%, the shear modulus increases with a decrease of $\bar{M}_n$ of the oligomer, that is, with an increasing crosslinking density, which follows the theory of rubber-like elasticity. At the same time, the shear modulus of 10% gels starts to decrease when $\bar{M}_n$ decreases below a certain value ($\bar{M}_n \sim 5000$). Simultaneously, as is seen from *Figure 9*, when the concentration of gels (in the oligomer region of $\bar{M}_n$ of 1000–5000) is $\leqslant 10\%$, a considerable static creep is seen. For equiconcentrated gels at greater M_n's (of the crosslinked oligomer) this creep is absent.

These peculiar properties of weakly concentrated gels indicate that below a certain $\bar{M}_n$ of the oligomer the actual distances between the crosslinks is becoming greater and

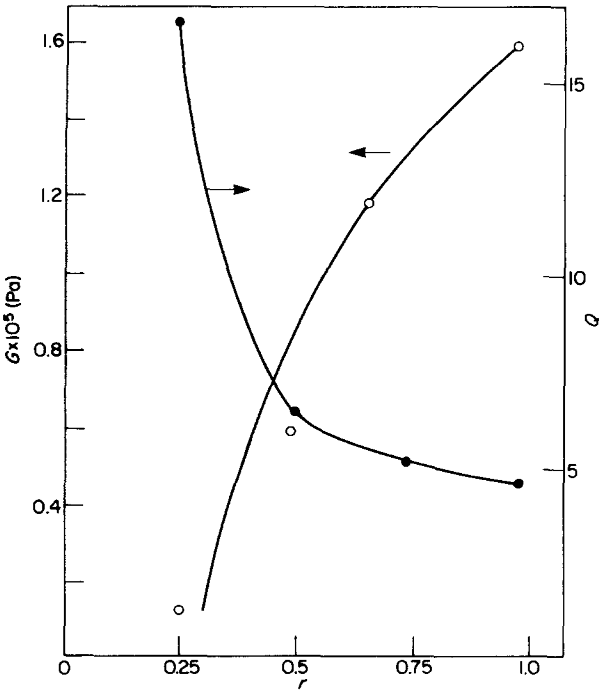

Figure 5 Dependence of the shear modulus and the swelling degree on the molar ratio of the crosslinking agent to the oligomer being crosslinked, *r*

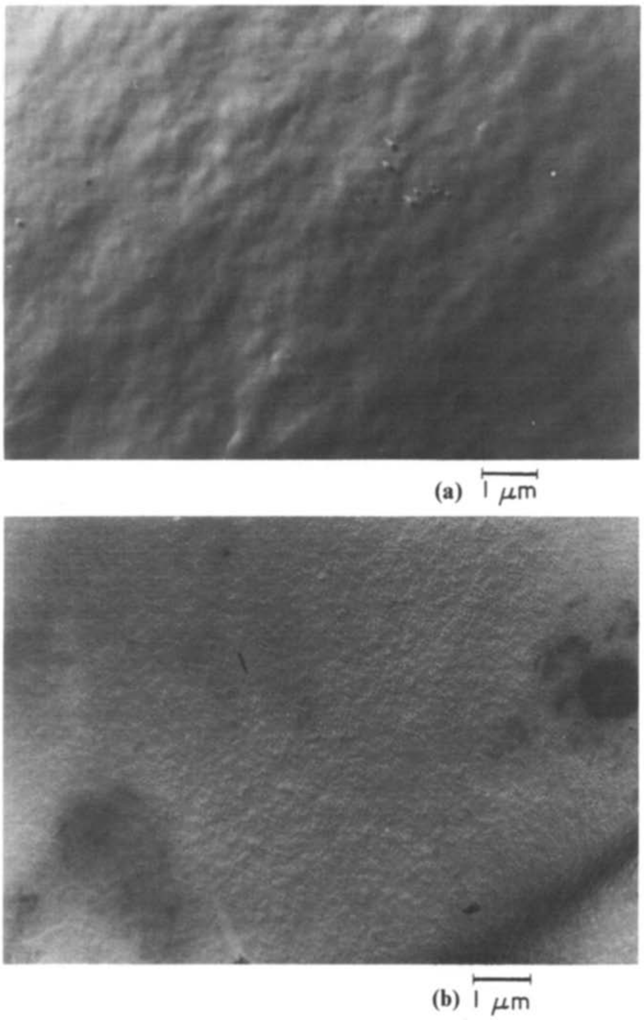

Figure 6 Electron micrographs of 'dry' siloxane networks prepared in the absence and in the presence of the solvent: a: $v_0=1$; b: $v_0=0.05$

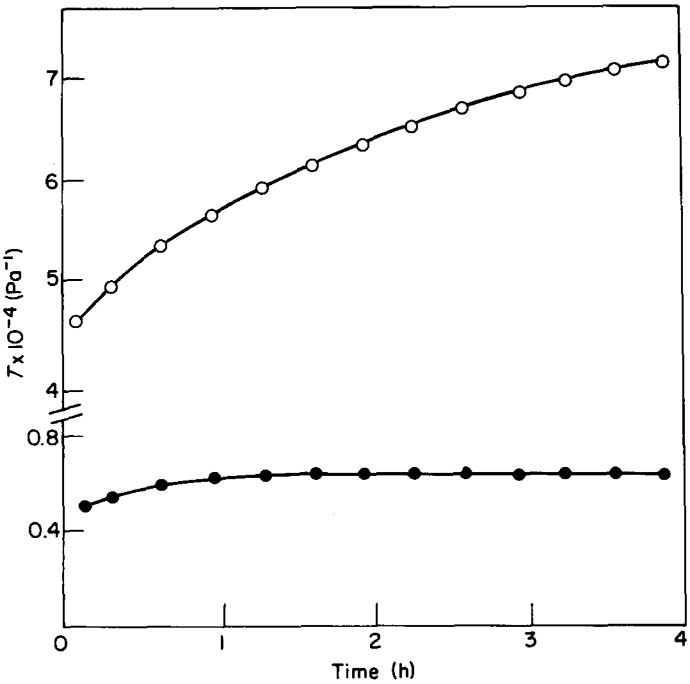

Figure 7 Creep of 5% gels prepared by polycyclotrimerization of 4,4-diphenylmethane diisocyanate in various solvents; (○): in *N*-methylpyrrolidone; (●): in anisole

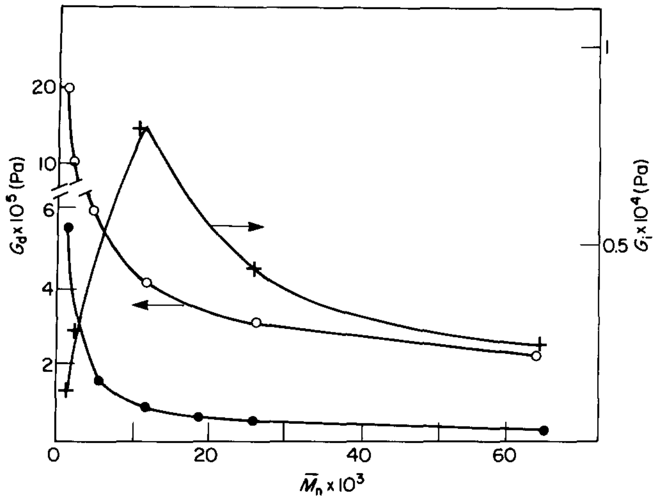

Figure 8 Dependence of the shear modulus of siloxane networks upon the molecular mass $\bar{M}_n$ of the polymer being crosslinked; (+): 10% original gel in heptane; (○): the network formed in the absence of the solvent; (●): the same network swollen to equilibrium

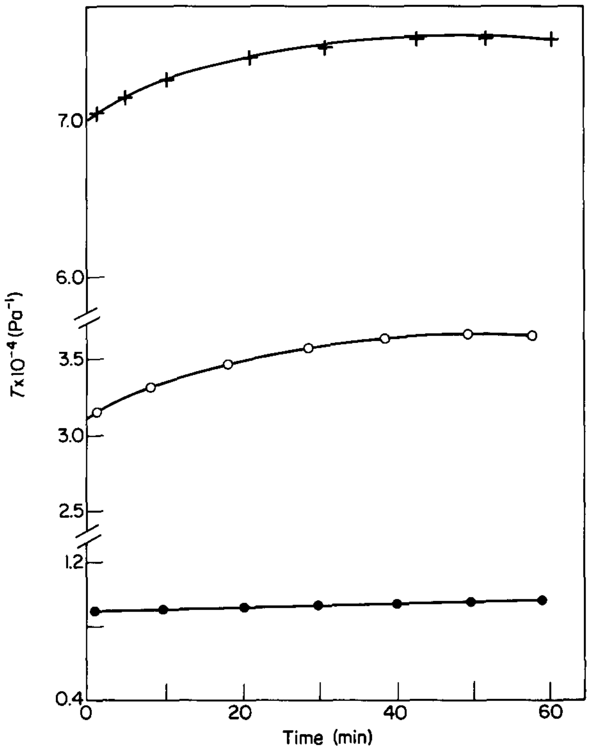

Figure 9 Compliance of 10% siloxane gels prepared by crosslinking in solution, at $\bar{M}_n$ of oligomer; (+): 970; (○): 2080; (●): 11 000

thus the network in the gels, with a decrease of $\bar{M}_n$, becomes looser rather than more dense. It means that the actual value of M_c of the network does not any longer agree with the value of $\bar{M}_c$ of the oligomer being crosslinked.

Such changes in the network parameters can result from the fact that part of the functional groups are used for ring formation and $\bar{M}_n$ corresponds to the sum of the distance between them and the size of the ring itself. If this assumption is valid, then the data obtained show that the degree of the intramolecular cyclization increases with decreases in the molecular mass of the oligomer being crosslinked. This is in good agreement with the experimentally established behaviour for the formation of

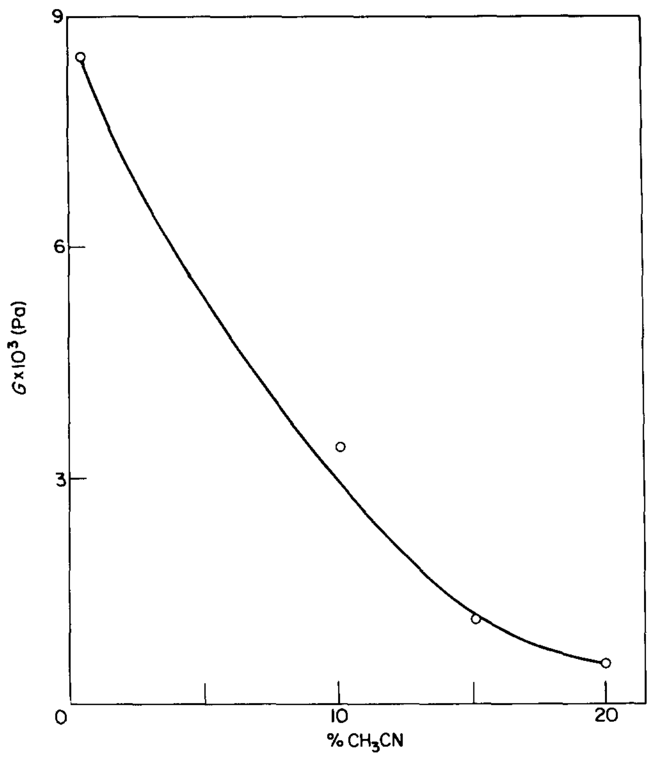

Figure 10 Dependence of the shear modulus of 10% siloxane gels upon the amount of the non-solvent in the mixture in which the network is being formed

crosslinked polyurethanes upon changing $\bar{M}_n$ of the oligoglycols[28]. It also agrees with the theoretical estimates of the process of polyfunctional polycondensation[29]. At the same time, on crosslinking of the prepared chains the degree of intramolecular cyclization increases with an increase of the molecular mass[30].

The effect of the solvent quality upon the gel properties

Thermodynamic quality of the solvent influences differently the properties of both types of the networks investigated. *Figure 10* shows that when siloxane is formed in a mixture of the solvent (toluene) and the non-solvent (acetonitrile), and the non-solvent content is increased, the shear modulus of the 10% one-phase gel decreases. When the amount of acetonitrile is increased, phase separation of the system occurs, resulting in turbidity, syneresis and a porous gel structure. This structure is retained even after the solvent is removed, though the total pore volume is not large, being equal to 0.09 $cm^3\ g^{-1}$. Therefore, it is possible to obtain a porous structure in all poor solvents (in which the original linear polymer is at the point of precipitation). This also occurs in rubber-like elastic networks despite great shrinkage typical of them[31]. If the concentration of the crosslinked oligomer is increased and its molecular mass decreased (to give a higher network density), the amount of non-solvent required for the onset of phase separation can be decreased. This agrees well with theory[20].

The shear modulus of siloxane networks increases when the solvent is improved; however, when we consider polyisocyanurate networks the shear modulus increases with a deterioration of the solvent quality. *Table 3* shows that the shear modulus of 5% gels in anisole is significantly more than in *N*-methylpyrrolidone.

This is directly connected with an independently established increasing role of cyclization in poor solvents (in the case of poly(dimethylsiloxane)s)[32] and in good solvents (in the case of polycyanurates)[24].

The different manifestation of solvent quality for the gels obtained on the basis of flexible and rigid networks can be accounted for by the fact that in siloxane networks with rather weak intermolecular interaction, the solvent primarily influences the conformation of macromolecules. But in polyisocyanurates it influences the degree of aggregation, which is due to considerable intermolecular interaction. In the latter case solvation effects play a very important role.

A substantial decrease of the number of actual crosslinks in the network with a change of the nature of the solvent in poly(isocyanurate) gels, results in sharp changes of the rubber-like elasticity of the gels as is seen in *Figure 7*. As a result, after the solvent is removed, the porosity of dry gels also sharply changes. The total volume of the pores in the network (V_{total}) obtained from the rubber-like elastic gel in a good solvent (*N*-methylpyrrolidone) is equal to 0.095 $cm^3\ g^{-1}$ (due to a considerable shrinkage), the total volume of the pores in the network obtained from the rigid gel in a poor solvent (anisole) $V_{total} = 0.365\ cm^3\ g^{-1}$. It is quite natural that these differences in the porosity of 'dry' networks cannot exhibit themselves in their rheological properties.

Dependence of properties of 'dry' networks upon the conditions of their formation in a solvent medium

It follows from the data given in *Tables 2* and *3* that the shear modulus of 'dry' siloxane networks decreases more than 20 times in the investigated range of concentrations at which the network is formed in solution. The shear modulus of 'dry' polyisocyanurate networks decreases by more than two orders of magnitude.

The decrease of the shear modulus of 'dry' networks formed in solution results from the difference in their reference states. In fact, for the network obtained in the dry state it is this very state which is the reference state, the line-sizes of the chains on the formation of the network being unchanged compared with the initial ones. As to the network obtained in solution in a swollen state, the conformations of the chains are disturbed by the solvent and this particular state is the reference one. During the process of removing the solvent, the chains become coiled, thus leading to alternative conformations of the chains due to the presence of crosslinks. These conformations which are not produced in the absence of a solvent are

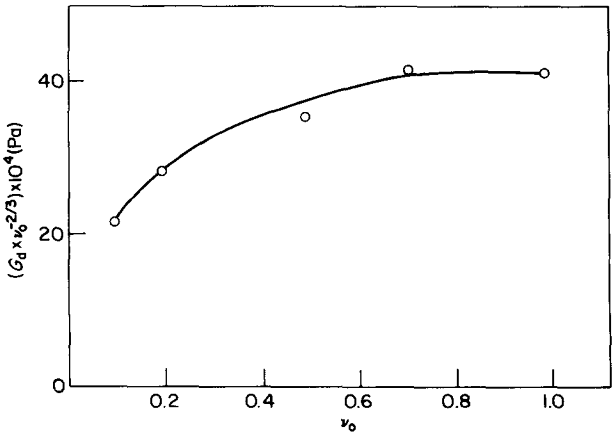

Figure 11 Dependence of $G_d v_0^{-2/3}$ upon the concentration of the network formation in solutionv_0

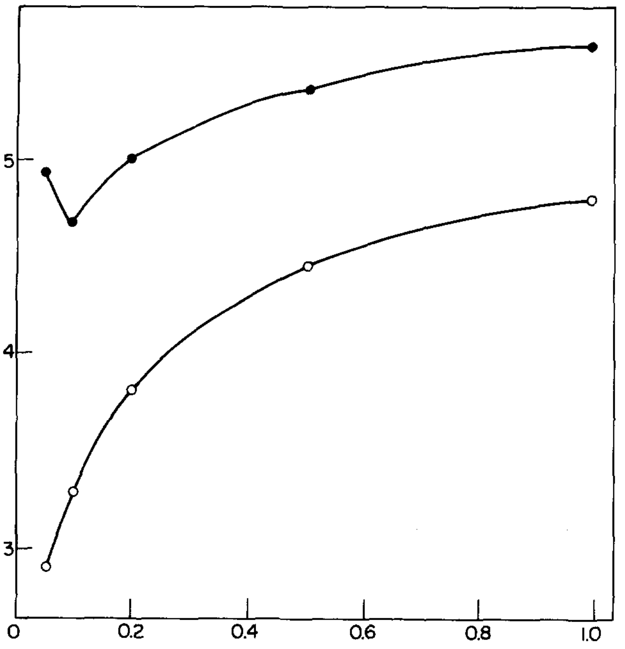

Figure 12 Dependence of the shear modulus of 'dry' siloxane networks upon the concentration of the polymer in gel v_0; (○): the gels swollen to equilibrium; (●): 'dry' networks prepared by removing the solvent from the gels swollen to equilibrium

called 'supercoiled' conformations[33]. The smaller the concentration at which the network is formed in solution, the greater the changes in the chain sizes. The ratio of the sizes of the network chains and those in a free state determines the value of the front-factor in the expression correlating the elastic force and the network deformation[1], that is, the shear modulus is proportional to $v_0^{2/3}$. Accordingly, the ratio of the shear modulus of the dry network (formed in solution) to $v_0^{2/3}$ should be a constant value, and equal to the shear modulus of the network obtained without a solvent. This was, in fact, proved experimentally for a number of different networks when the concentration of the polymer being crosslinked exceeded 40%[34], and even for polystyrene networks at $v_0 = 7\%$[8].

Figure 11, however, shows that in case of siloxane networks the value $GV_0^{-2/3}$ is not constant: it decreases slightly down to $v_0 = 0.5$ and drops very sharply when the networks are formed at considerably high dilution. It is again indicative of the fact that the network structures obtained in solution and without a solvent markedly differ from each other, which is not taken into account in the theory of rubber-like elasticity. This is due to high porosity of the networks, which increases with a decrease of concentration at which they are formed in solution, this porosity being retained upon removal of poor solvents and disappearing to a considerable degree due to shrinkage upon removal of good solvents. A great number of intramolecular bonds thus formed and variations in 'statistical quality'[35] of the network chains largely contribute to variations in the network structure.

All the above factors can increase the chain packing density due to conformational changes. With an increase of the rubber-like elasticity of the original gel and a decrease of its concentration, the increase of the packing density of the network chains on the removal of the solvent is more intensive. Therefore it is obvious that this increase of the packing density is responsible for the fact that in low-crosslinked siloxane networks prepared at concentrations of 5–10%, a decrease in the shear modulus of the dry network with a decrease of the initial concentration is replaced by an increase in the shear modulus (as seen from *Figure 12*), while for the gels themselves this extreme change of the modulus does not occur.

Variation in the structure of the crosslinked polymers during solvent removal (followed by shrinkage and increasing of packing density of the network largely determined by the rate of drying) also results in a marked decrease of its ability to absorb the solvent. As was shown in ref. 36 for polystyrene–divinylbenzene networks obtained at dilutions not exceeding 50%, the equilibrium swelling of the networks after the removal of the solvent is completely reversible. However, in siloxane networks, as can be seen from *Table 2*, the repeated swelling of the networks obtained at any solution concentration is always less than that of the original gels. This difference is largest when the network is obtained at high dilution: the swelling of dry siloxane networks obtained at 5% concentration is 3–4 times less than that of original 5% gels and less than the swelling of networks obtained in the absence of the solvent. A similar effect is known only for butadiene–nitrile rubber vulcanized in 7% solution[37]. It is obvious that this is promoted by the rubber-like elasticity of the original gels. Even in case of relatively rigid and highly crosslinked polyisocyanurate networks which form rubber-like elastic gels in a good solvent, the irreversible swelling has the same order of value. Thus one can assume that rubber-like elasticity of the polymeric body contributes to such a dense packing of the network chains which cannot be completely destroyed by the interaction with the solvent.

The above peculiarities of the properties of dry networks directly affect the character of variations in their density. *Figure 13* shows that though the density of the initial siloxane gels decreases with a decrease of their concentration, the density of the 'dry' networks obtained

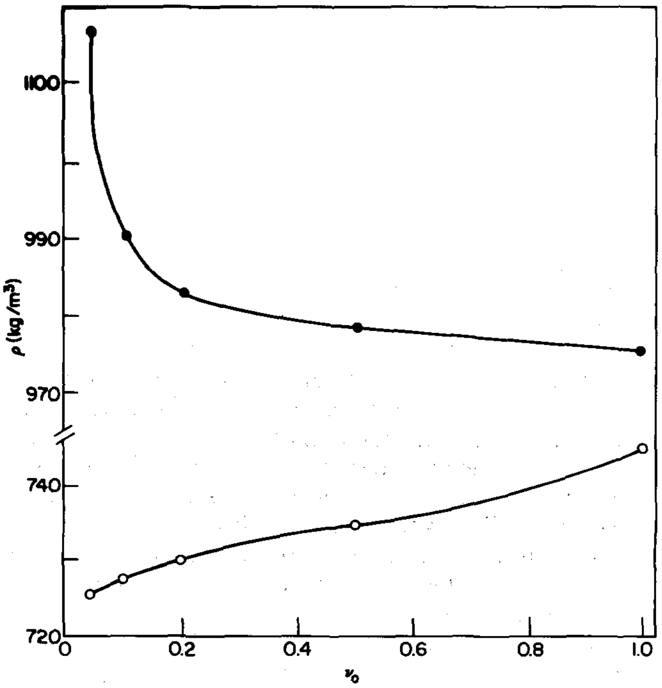

Figure 13 Dependence of the density of the original siloxane gels (○) and the 'dry' networks obtained from them (●) upon the concentration at which the network is formed, v_0

from them increases, especially in the region of high dilutions (> 10% of the polymer). Thus it follows that the 'dry' crosslinked polymers obtained in the state of diluted gel have greater density than those formed in the absence of the solvent.

Such a great increase of the polymer density (by 2%) can be accounted for only by a very considerable improvement of the packing density of macromolecules crosslinked in solution, the packing being very similar to that of crystalline polymers. However, the period of identity measured by X-ray technique does not change in this case.

It is worth noting that an increase in density depends upon the amount of tetraethoxysilane taking part in the crosslinking reaction of α,ω-dihydroxyoligodimethyl siloxanes in solution, that is, it increases with an increase of the latter. Since an increase in the amount of tetraethoxysilane is usually followed by an increase in the amount of organotin catalyst, it is possible to assume that an increase in the density of the crosslinked polymer is due to absorption of tin traces not removed during the washing out process. However, in a similar way, an increase of the amount of the crosslinking agent increases the shear modulus of the 'dry' networks, but the shear modulus is not affected by the amount of tin. *Figure 14* shows that such an increase of the elastic modulus takes place despite the fact that the shear moduli of the original gels change markedly and decrease with increasing amounts of the crosslinking agent more than the stoichiometrical one. This is typical for networks obtained from the process of polyfunctional polycondensation[22].

The results considered above lead to the conclusion that during solvent removal some additional chemical bonds are formed, which are the result of the presence of a great number of free chain terminals formed during the sysnthesis of the networks in solution. The number of these bonds exceeds the number of bonds produced when crosslinking occurs in the absence of the solvent.

It is of interest that in case of polyisocyanurate networks with the original diisocyanate of small size (high crosslinked networks and great intermolecular interaction), the density of the 'dry' network considerably decreases with increasing dilution at synthesis, as is seen from *Figure 15*. It is obvious that it is caused by a decrease in the intermolecular interaction in solution, which interferes with the dense packing of the network chains. With an increase in the size of the diisocyanate molecule on passing over to macrodiisocyanate on the basis of oligo(propylene glycol) and toluylene diisocyanate, the network by its behaviour resembles the siloxane network with flexible chains, and the density of this network also increases with an increase of the initial dilution.

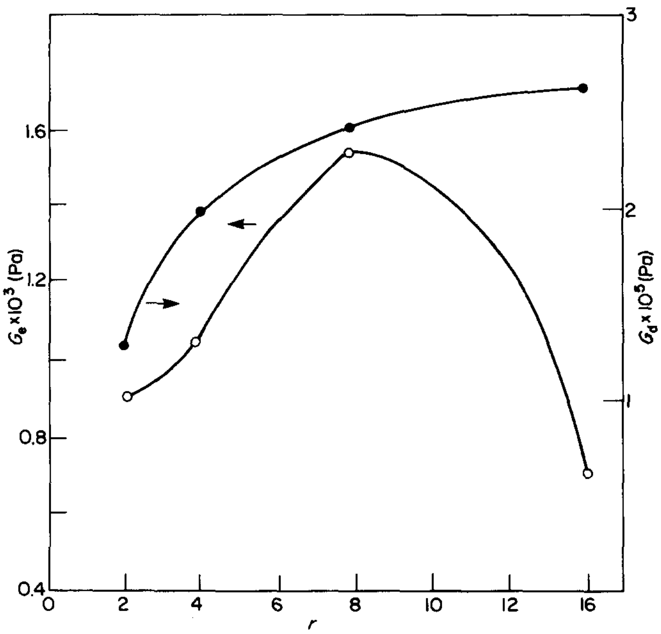

Figure 14 Dependence of the shear modulus of siloxane networks upon the molar ratio of the crosslinking agent and the oligomer, r (○, initial gel and ●, dry network)

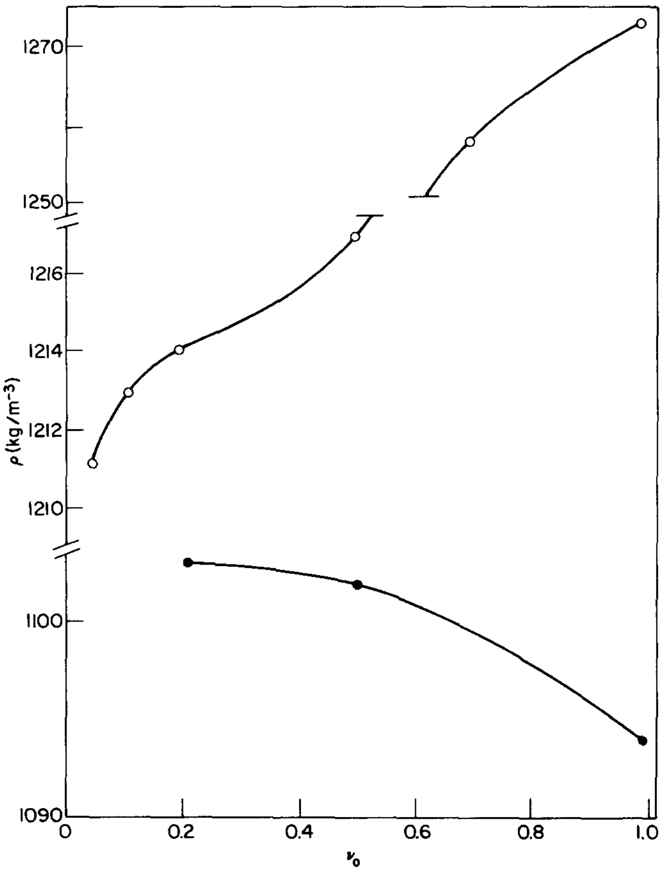

Figure 15 Dependence of the density of 'dry' polyisocyanurate networks upon the concentration at which the network is formed; (○): network based on 4,4-diphenylmethane diisocyanate, $M_c = 242$; (●) network based on macrodiisocyanate $M_c = 1600$

CONCLUSION

Investigation of the dependence of the properties of two types of chemical networks (differing in the flexibility of chains, intermolecular interaction and crosslinking density) on the conditions of their formation in solution (amount and thermodynamic quality of the solvent) has shown that viscoelastic properties and swelling ability of the gels being formed and the dry networks obtained from them change in a very wide range. The results have shown that there is a marked difference between the networks formed in the absence of the solvent and in solution. These results confirm that the gels appear to be frozen systems in which the properties of the final ensemble are defined by the properties of the preparative ensemble[19]. The changes in the properties of the networks found in the present work appeared to be much greater than those predicted by the theory of rubber-like elasticity for the networks formed in solution, which is indicative of a considerable difference between the mechanism of formation and structure of such networks and the networks formed without a solvent.

ACKNOWLEDGEMENT

The authors thank Professor V. A. Pankratov and Dr Ts. M. Frenkel for the synthesis of polyisocyanurates and to Dr E. A. Obolonkova for the preparation of electron micrographs.

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