

Study of three-dimensional polystyrene networks containing linear chains:

1. Influence of free chains on the volume fraction of crosslinked chains

F. Rietsch, A. Brault[†] and D. Froelich[†]

Laboratoire de Structures et Propriétés de l'Etat Solide, Université des Sciences et Techniques de Lille, 59650 Villeneuve d'Ascq, B.P. 36, France

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A ternary system, crosslinked polystyrene—linear polystyrene in swelling equilibrium in benzene or cyclohexane, has been prepared by anionic polymerization in dilute solution (7.5%). By swelling ratios and modulus measurements we proposed to show the specific influence of linear polystyrene chains of high molecular weight, maintained inside the network, and to compare this behaviour with the behaviour of an 'ideal' polystyrene network. It may be concluded that: (i) the calculated number of elastic chains is independent of the swelling solvent, but the presence of free chains in the polymerization and crosslinking process produces a non-negligible number of free and pendant chains; (ii) for the same number of elastic chains, the two types of networks have the same swelling ratio, but the introduction of free chains into the networks leads to a decrease in the volume fraction of crosslinked chains, and thus to an increase in the swelling rate of the network. However, these values are consistent with the Gaussian theory; (iii) the values of functionality are lower than those found for 'ideal' networks; this result confirms the presence of pendant chains; (iv) the Flory—Huggins parameters are the same for the two types of networks.

INTRODUCTION

The study of three-dimensional polymeric networks has been the subject of much research from the theoretical point of view as well as from the experimental. To ensure a better control of these networks we made use of an anionic polymerization method developed by Rempp and coworkers¹⁻³ which should make it easier to understand crosslinks in relation to the properties of the networks.

In studies of model crosslinks of fairly well defined chemical structure, most of the research has dealt with their physicochemical properties so as to determine the structural parameters^{4,6}. These measurements were mainly taken in good solvents in which the stress relaxation for polymer chains is short. These ideal polystyrene networks helped us to acquire a good knowledge of the structure in relation to the molecular parameters which control the physicochemical properties of these gels. Using these results, we have tried to show the specific influence of linear polystyrene chains of high molecular weight, maintained inside the network, whose porosity is sufficiently low as to make all diffusions out of the network negligible⁷.

Here, we propose to study more particularly the influence of free chains on the swelling ratio of the network. A study of ternary solutions of crosslinked polystyrene, linear polystyrene and toluene, shows that when the molecular weight of linear chains is too high to allow diffusion into the network, the volume fraction of the gel decreases⁷. It is therefore feasible to suppose that when linear chains

are confined inside the network, the inverse phenomenon takes place.

The calculation for the variation of free energy in elastic deformation, ΔF , has raised much controversy and leads to the following general equation:

$$\Delta F = \frac{\Delta v_e k T}{2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) - B v_e k T \lambda_x \lambda_y \lambda_z$$

in which v_e represents the number of elastic active chains; $\lambda_x, \lambda_y, \lambda_z$, are the deformation ratios projected on three reference axes; k and T are the Boltzmann constant and the absolute temperature (K), respectively. According to Flory, Wall and Hermans, $A = 1$ and $B = 2/f$ where f represents the mean functionality of the crosslinks. When a crosslink is at swelling equilibrium in a solvent, the chemical potential on either side of the network is defined by the equation:

$$\frac{\Delta v}{RT} = A v_e^* R T \bar{v}_1 q_0^{-2/3} v_2^{1/3} - B R T v_e^* \bar{v}_1 v_2 + RT |\log(1 - v_2)| + v_2 + \chi v_2^2 = 0 \quad (1)$$

where \bar{v}_1 = partial molar volume of the diluent; $v_2 = q_i^{-1}$ = volume fraction of the non-deformed network; v_e^* = number of moles of network chains per unit dry polymer volume; χ = the Flory—Huggins interaction parameter;

$$q_0^{2/3} = \frac{\langle r_{OS}^2 \rangle}{\langle r_D^2 \rangle} = \frac{\langle r_{OS}^2 \rangle}{\langle r_C^2 \rangle} q_C^{2/3}$$

[†] Present address: Ecole d'Application des Hauts Polymères, 4, rue Boussingault, 67000 Strasbourg, France.

Table 1 Network characterization by measurement of molecular weights from linear chains

Gel	Free chains (%)		\overline{M}_n	\overline{M}_w	$\frac{\overline{M}_w}{\overline{M}_n}$
	Crosslinked chains				
1912	0.0		16 300	17 800	1.09
1112	2.5		18 800	20 700	1.10
2711	5.0		18 700	20 700	1.11
612	7.5		16 000	17 900	1.12
412	10.0		18 500	21 100	1.14
1712	12.5		16 200	18 600	1.15

where $\langle r_{OD}^2 \rangle$ and $\langle r_{OS}^2 \rangle$ = mean square end-to-end distance of network chains in the dry and swollen reference states, respectively; $\langle r_D^2 \rangle$ and $\langle r_C^2 \rangle$ = mean square end-to-end distance of network chains in the dry state and after crosslinking; q_0 = the swelling of the gel in the swollen reference state. q_0 is called the 'memory term' as it is linked to q_C^{-1} , the volume fraction of the polymer at the crosslinking stage. Later in this study we point out that two gels prepared under the same experimental conditions (even q_C) are characterized by the same values of q_0 .

When the swollen gel undergoes a unidirectional stress (force per unit swollen and stained cross-section) either elongation ($\Lambda_x > 1$) or compression ($\Lambda_x < 1$), its degree of swelling will change from q_i to q . Equation (1) yields:

$$\sigma = Aq_0^{-2/3}q_i^{-1/3}\nu_e^*RT\left|\Lambda_x^2 - \frac{q}{q_i}\Lambda_x^{-1}\right| \quad (2)$$

$\Lambda_x = L/L_i$ where L_i is the initial length of the sample swollen at equilibrium and L is the stressed length of swollen sample. q is the swelling ratio at stress equilibrium. It has been shown⁵ that when the stress σ equals the instantaneous stress σ_0 obtained after deformation, equation (2) can be written:

$$\sigma_0 = Aq_0^{-2/3}q_i^{-1/3}\nu_e^*RT\left|\Lambda_x^2 - \Lambda_x^{-1}\right| \quad (3)$$

in which

$$\sigma_0\left|\Lambda_x^2 - \Lambda_x^{-1}\right|^{-1} = Aq_0^{-2/3}q_i^{-1/3}\nu_e^*RT$$

represents the experimental modulus G_{ex} .

EXPERIMENTAL

Polystyrene gels were prepared by anionic copolymerization of styrene and divinylbenzene (DVB) following the method of Rempp and coworkers¹⁻³.

So as to make these gels comparable with those serving as criteria for comparison^{5,6}, we chose a polymer concentration $q_C^{-1} = 7.5\%$ and a proportion of 3 DVB/living end at the crosslinking stage. The molecular weight between crosslinks was chosen to be between 15 000 and 20 000. This offered the advantage of giving gels with better mechanical properties than those of high molecular weight, and crosslinking times which were long enough to ensure good homogeneous samples. The free chains were therefore present during the homopolymerization of the styrene and were confined to the network during the crosslinking process. They were prepared anionically, with a molecular weight $\overline{M}_n = 810\,000$ and a polydispersity $\overline{M}_w/\overline{M}_n = 1.38$.

In *Table 1* we have listed the molecular weight between crosslinks for the different samples and the weight ratio of free chains to crosslinked chains.

It is to be noted that the polydispersity increases slightly with the number of free chains present at the moment of polymerization. This is certainly due to the increase of viscosity in the reactor. Copolymerization of styrene-DVB is to be expected because of the presence of free chains.

From the equation for chemical potential (equation 1), the network can be defined by four parameters: the number of active elastic chains; the memory term; the functionality; the polymer-solvent interaction parameter. These can be determined by measurements of modulus and volume fraction of the polymer in two solvents: benzene and cyclohexane⁵.

The volume fractions obtained are shown in *Table 2*.

We can define the volume fraction of the crosslinked polymer with no free chains, v_2 , as follows:

$$v_2 = \frac{V_2}{V_1 + V_2}$$

where V_1 and V_2 are volumes of the solvent in the swollen polymer and of the crosslinked polymer chains, respectively. The volume fraction of the crosslinked polymer with free chains present becomes:

$$v_2 = \frac{V'_2 + V_3}{V'_1 + V'_2 + V_3}$$

and the volume fraction of the crosslinked polymer only:

$$v'_2 = \frac{V'_2}{V'_1 + V'_2 + V_3}$$

where V_3 = the volume of free chains contained in the network. The results in *Table 2* show that the swelling ratio in benzene is not directly related to the percentage of free chains. This cannot be explained by the differences in the molecular weights between crosslinks of the various samples. In cyclohexane and methyl cyclohexane, the swelling ratios are very similar. In conclusion, this technique does not assist in showing any specific influence of the free chains present in the network.

In *Table 3* are given the values of the modulus in cyclohexane and in benzene at 20°C, as well as the number of elastic chains calculated from the relation:

$$\nu_e^* = \frac{G_{ex}}{ARTq_0^{-2/3}\nu_2^{1/3}}$$

with $q_0^{-2/3} = 0.127$ and $A = 1$.

Table 2 Volume fractions obtained from swelling ratio measurements in benzene and cyclohexane

Gel	Free chains (%)	Benzene, $v_2 \times 10^2$	Cyclohexane, $v_2 \times 10^1$
1912	0.0	4.54	2.35
1112	2.5	3.85	2.06
2711	5.0	5.12	2.44
612	7.5	4.34	2.33
412	10.0	4.46	2.33
1712	12.5	4.77	2.35

Table 3 Number of experimental and theoretical elastic chains

Gel	Benzene		Cyclohexane		
	G_{exp} (dyne/ cm ²)	$\nu_e^* \times 10^5$ (mol/ cm ²)	G_{exp} (dyne/ cm ²)	$\nu_e^* \times 10^5$ (mol/ cm ²)	$\nu_e^* (= \rho/\overline{M}_n) \times 10^5$ (theor) (mol/cm ²)
1912	49 000	4.69	94 000	5.17	6.44
1112	31 500	3.19	70 000	3.71	5.59
2711	67 000	6.17	108 000	5.91	5.61
612	49 000	4.62	82 000	4.42	6.56
412	55 000	5.36	85 000	4.73	5.68
1712	63 000	5.94	101 000	5.60	6.48

The final column of *Table 3* represents the number of theoretical elastic chains given by the equation $\nu_e^* = \rho/\overline{M}_n$, where ρ is the density of the dry polystyrene and \overline{M}_n the molecular weight between crosslinks, given in *Table 1*.

In order to take modulus measurements, the samples were in solvent equilibrium in a parallelepiped glass cell at ambient temperature, and in a cylindrical brass cell for measurements taken at varying temperatures. Elongation was measured by a cathetometer with a precision of 1/20 mm. A calibrated inductive transducer (Model Q11/100 gP Hottinger Balwin) was used to measure the stress. Thickness was measured by a microscope with a precision of $\pm 5/1000$ mm, and other measurements were taken by means of slide calipers with a precision of 1/20 mm. The elasticity moduli were determined to a precision of $\pm 2.5\%$. For each measurement we allowed 3 days thermic conditioning to obtain the necessary swelling equilibrium.

DISCUSSION

Number of active elastic chains

For similar samples, the difference in the number of elastic chains in the two solvents is within the experimental precision (6%). We can therefore state that the number of elastic chains is independent of the solvent, which is consistent with theory⁵. On the other hand, the calculated number of elastic chains is lower than the number of theoretical chains. This is an important phenomenon, since it shows that the presence of free chains in the polymerization and crosslinking processes produced a non-negligible number of free and pendant chains. It is possible to extract free chains of low molecular weight by successive washings in a good solvent, but the pendant chains remain in the network, and this consequently decreases the number of elastic chains and even the modulus itself. This can be explained qualitatively by the increase in viscosity during polymerization and at the crosslinking stage.

Swelling ratios

So as to determine the influence of pendant and free chains (of high molecular weight) on swelling ratio, we compared these networks with 'ideal' networks having the same number of elastic chains⁵, as shown in *Figure 1*. We can note that the two types of networks have the same swelling ratio for the same number of elastic chains.

This swelling ratio is defined as follows:

$$Q'_i = \frac{V'_1 + V'_2 + V'_3}{V_2 + V'_3}$$

in which V'_1 , V'_2 and V'_3 are the volumes of the solvent, the network and the free chains in the swollen sample, respectively; that is, the inverse of the volume fraction of the total polymer in the swollen gel.

For an 'ideal' network with no free chains, this swelling ratio is defined by the equation:

$$Q_i = \frac{V_1 + V_2}{V_2}$$

If this 'ideal' network has the same number of elastic chains as the network containing free chains, we can note experimentally that the two types of gels will have the same swelling ratio: that is:

$$Q_i = Q'_i$$

Let us also suppose that the volume of the crosslinked polymer in the two networks is the same, that is:

$$V_2 = V'_2$$

We then obtain the relation:

$$\frac{V'_1 - V_1}{V_1} = \frac{V'_3}{V_2}$$

which means that the volume increase of the solvent in the swollen network is proportional to the number of free chains included in the network.

Thus the introduction of free chains into the networks causes such an increase in the quantity of solvent in the swollen gels that the volume fraction of the polymer, that is to say of crosslinked and linear chains remains constant. This clearly leads to a decrease in the volume fraction of crosslinked chains, and so an increase in the swelling rate of the network (*Figure 2*).

Swelling equilibrium of a Gaussian network

If we now compare the equations for the chemical potential in an ideal network and in a network containing

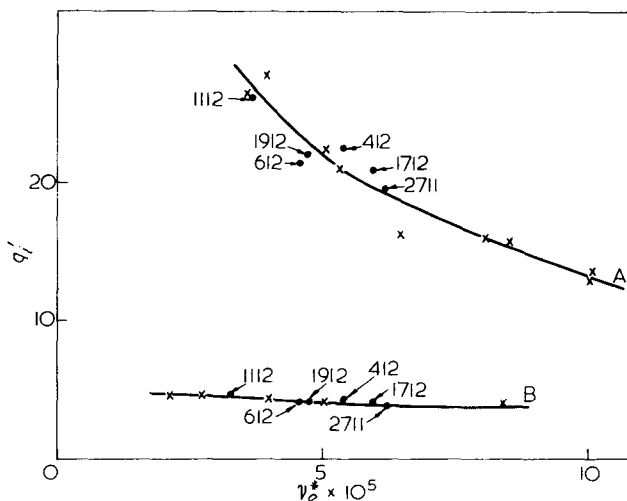


Figure 1 Apparent experimental swelling ratio, q'_i , versus ν_e^* , the number of moles of active network chains per unit dry polymer volume. A, Benzene; B, cyclohexane. +, Experimental values for ideal polystyrene networks⁵ in benzene and cyclohexane; ●, experimental values for ternary systems in benzene and cyclohexane

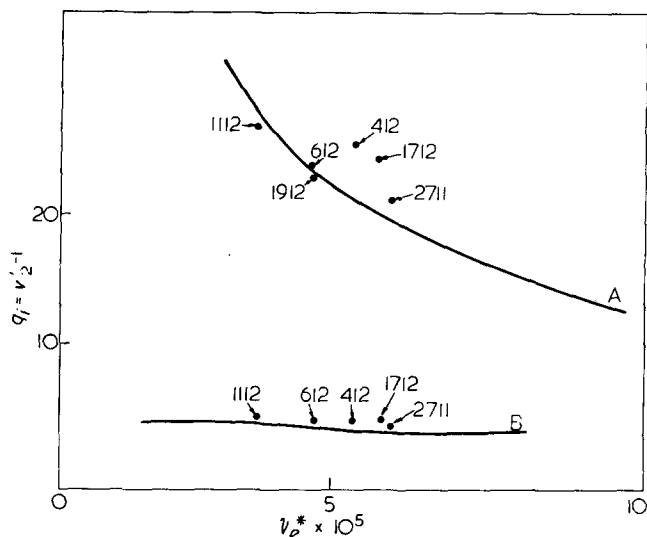


Figure 2 Experimental swelling ratio of the network only, $q_i = v_2' / v_2^{-1}$ versus v_e^* , the number of active network chains per unit dry polymer volume. A, Benzene; B, cyclohexane

free chains, we have for an ideal network:

$$\frac{\Delta v}{RT} = A \bar{V}_1 q_0^{-2/3} v_e^* v_2^{1/3} - B v_e^* \bar{V}_1 v_2 + \log(1 - v_2) + v_2 + \chi_{12} v_2^2 = 0 \quad (4)$$

and for a network with the same number of elastic chains, and containing a volume fraction v_2' of crosslinked chains and v_3 of linear chains we obtain:

$$\frac{\Delta v}{RT} = A \bar{v}_1 q_0^{-2/3} v_e^* v_2'^{1/3} - B v_e^* \bar{V}_1 v_2' + \log(1 - v_2' - v_3) + (v_2' + v_3) + \chi_{12} (v_2' + v_3)^2 = 0 = X + Y \quad (5)$$

where X and Y are the elastic and dilution terms, respectively. In this relation we suppose that $\chi_{12} = \chi_{13}$.

If the two types of networks have the same swelling ratio for the same number of elastic chains (Figure 1), then:

$$v_2' + v_3 = v_2$$

and it follows that equations (4) and (5) have the same dilution term Y .

A calculation for gels containing the highest percentage of free chains, gave the same elastic X term, within the experimental precision (3%), for the two types of networks in swelling equilibrium in benzene.

We can therefore see that the values of the swelling ratios of the different samples are consistent with theory (equations 4 and 5). As the free chains have little influence on the elastic term of the equation for the chemical potential, it will clearly be the same for the dilution term; this leads to swelling rates which are the same for networks containing free chains and for ideal networks.

Table 4 Physicochemical characterization

Gel	Free chains	$Bv_e^* \times 10^5$	f	χ_{12} Benzene
1912	0.0	2.37	4.36	0.471
1112	2.5	2.20	3.37	0.479
2711	5.0	2.49	4.75	0.468
612	7.5	2.11	4.19	0.462
412	10.0	2.13	4.44	0.458
1712	12.5	2.58	4.34	0.461

Flory-Huggins interaction parameter and functionality of crosslinks

The variation of χ_{12} in cyclohexane with the volume fraction of polymer and temperature is well known in the case of linear polystyrene. Moreover, as the structural parameter is of little importance in the case of low swelling ratio⁵, we can take it that the interaction parameter for crosslinked polymer-solvent is the same as that for the linear polymer-solvent parameter.

We made use of the Scholte equation⁸, which is valid for a range of concentration close to that we encountered in the gels:

$$\chi_{12} = \chi_{13} = 0.2975 + \frac{62}{T} + 0.306 q_i^{-1} + 0.300 q_i^{-2}$$

Using this value in equation (5) we can calculate Bv_e^* and deduce the value of functionality, $f = 2/B$. In Table 4 we give the values of Bv_e^* and f .

The values of functionality are lower than those found for 'ideal' networks⁵; this result confirms the presence of pendant chains in our networks.

Using the f values in equation (4), we can calculate the interaction parameter χ_{12} in the case of benzene if we consider that χ_{13} , the interaction parameter for linear polystyrene-solvent in the ternary system is the same as the interaction parameter in the case of a binary polystyrene-benzene system, that is: $\chi_{13} = 0.456$ (ref 9).

In Table 4 we give the values of χ_{12} calculated for the crosslinked polystyrene-benzene system. These values are consistent with those found for 'ideal' networks, that is: $0.468 < \chi < 0.479$.

The small difference between the values of χ_{12} and χ_{13} shows that the swelling ratio of the 'crosslinked and linear polystyrene' system is in good correlation with the swelling rate of 'ideal' networks.

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