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Interpretation of equilibrium swelling data on model networks using affine and 'phantom' network models

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Well-defined polystyrene model networks and poly(dimethylsiloxane) model networks have been synthesized by endlinking processes under standard conditions. The networks have been swollen to equilibrium in appropriate swelling solvents. The experimental swelling data have been compared with those arising from the affine model and the 'phantom' model. The results obtained allow us to calculate the interaction parameter between the swelling solvent and the network. This coefficient strongly depends upon several structural parameters, such as the functionality of the crosslinks, the molar mass of the elastic chains, the polymer volume fraction upon crosslinking and the nature of the swelling solvent. In most cases, satisfactory agreement has been found between experiment and theoretical expectations. © 1997 Elsevier Science Ltd.

(Keywords: endlinking reactions; equilibrium volume swelling degree; interaction parameter)

INTRODUCTION

Swelling equilibrium and uniaxial compression–extension measurements are two basic experimental methods allowing us to characterize the behaviour of crosslinked polymer networks. The idea of swelling equilibrium was first introduced by Frenkel[1,2], and later developed by Flory and Rehner[3]. For a long time, the Flory–Rehner theory has been considered as a basic statement to evaluate the swelling degree Q of a polymer network swollen to equilibrium in a 'good' solvent (e.g. the polystyrene model network–benzene binary system[4]). In this model, swelling equilibrium results from a competition between two antagonistic effects which have been calculated *separately* by Flory and Rehner. The first contribution is related to the entropy of mixing between the network and its swelling solvent. It corresponds to the 'osmotic' pressure which tends to dilute the polymer chains, leading to a more extended configuration of the elastic chains of the network. In the presence of a solvent, these chains are partially free to move, contrary to what exists in the melt. The second contribution is due to an ensemble of rubbery retractive forces (e.g. the tridimensional response of rubber elasticity) which opposes the expansion of the network. It is connected with the elastic entropy change of the system arising from the deformation of the network induced by swelling. An equilibrium swelling state is eventually reached, in which the two antagonistic forces balance each other.

In its initial form, the Flory–Rehner theory[5] has allowed an interpretation of various experimental equilibrium swelling data on polymer networks[6–8]. In spite of its success, this theory has encountered numerous criticisms.

The description of the swelling theory of Flory–Rehner is based on the hypothesis of separability of the mixing and elastic free energies. The two terms have been calculated separately and it has been assumed that they are simply additive (and thus considered independent). The variation of the total free energy ΔF, associated with the change of volume induced by swelling, can be expressed as

$$\Delta F = \Delta F_{\text{dil}} + \Delta F_{\text{el}} \quad (1)$$

where ΔF_{dil} is the variation of the 'osmotic' free energy corresponding to the dilution of the polymer network chains and ΔF_{el} is the variation of the elastic free energy. However, these two terms are obviously connected by nature, since each of them depends upon the conformations of the chains. To test this point, improved experiments have been performed by Gee *et al.*[9] and by Eichinger and co-workers[10–14]. Differential solvent vapour and equilibrium swelling measurements have been carried out on natural rubber prepared by chemical reaction with dicumyl peroxide, swollen in benzene[9], and on poly(dimethylsiloxane) (PDMS) networks crosslinked by γ irradiation, swollen in benzene and in cyclohexane, respectively[10–12]. The experimental data obtained show that the variation of the reduced dilation modulus (experimentally accessible) vs the square of the deformation ratio λ expressed as

$$\frac{\lambda}{\overline{V}} \ln(\mu_{1,\text{c}}/\mu_{1,\text{u}}) = f(\lambda^2) \quad (2)$$

exhibits a pronounced maximum, contrary to the predictions of the classical theories of rubber elasticity[5,15–27]. In equation (2), $\overline{V}$ is the molar volume of the swelling solvent, $\mu_{1,\text{c}}$ is the activity of solvent on the swollen crosslinked polymer, and $\mu_{1,\text{u}}$ is the corresponding activity for the uncrosslinked polymer at the same concentration of solvent (the ratio $\mu_{1,c}/\mu_{1,u}$ represents the elastic contribution to solvent activity). The deformation ratio λ is defined as

$$\lambda = \left(\frac{v_c}{v_0}\right)^{1/3} \tag{3}$$

or obviously as

$$\lambda = \frac{V}{V_0} = Q \tag{4}$$

where v_c and v are the polymer volume fractions at which crosslinking took place and at swelling equilibrium, respectively, V is the volume of the isotropically swollen material and V_0 the volume in the dry state, and Q is the equilibrium volume swelling degree. From the data obtained by Brotzman and Eichinger[11,12], it results that the reduced swellability depends strongly upon the chemical nature of the swelling solvent. This observation suggests that the assumed additivity of the mixing and elastic contributions to the variation of the total free energy ΔF is questionable. Consequently, Eichinger and co-workers[10-14] have concluded that the Flory–Rehner theory requires some improvement. According to them, the solvent dependence may be explained by the introduction of an interconnecting term between the mixing and elastic terms of equation (1), although the expression of this additional term is not strictly formulated. Ultimately, it has been found that the Flory–Erman constrained junction fluctuation theory[28,29] accounts qualitatively for the data obtained with PDMS networks swollen in benzene and in cyclohexane, as swelling solvents, at 30°C.

However, Gottlieb and Gaylord[30] have reconsidered some of the data of Brotzman and Eichinger[11,12] on the basis of the Flory–Erman model[28,29]. As expected, the variation of the reduced dilation modulus vs λ^2 exhibits a well-defined maximum. But no agreement could be found between the experimental curves and the constrained junction fluctuation theory. However, the paper of Gottlieb and Gaylord[30] is more general. These authors have tried to compare the swelling data of Gee *et al.*[9] and those of Brotzman and Eichinger[11,12] with the predictions of new molecular theories, which are more and more sophisticated. In their paper, it is basically considered that the existence of a maximum on the plot of the reduced dilation modulus vs λ^2 is considered as a prerequisite for any theoretical model. Among the nine theoretical models investigated, five of them should be rejected (namely, the affine[5] and 'phantom' models[18-22,31], the potential pipe model of Edwards[32], the sliplink model of Ball *et al.*[33] and the primitive path model of Graessley[34]), since they do not satisfy the criterion of the maximum. On the contrary, a maximum is not incompatible with the tube model of Marrucci[35], the modified model of Graessley[34], the tube model of Gaylord[36-38] or the constrained junction fluctuation model described by Flory and Erman[28,29] (for more details, see reference 30). However, a quantitative agreement between the experimental swelling data on PDMS networks and those arising from the four latter models is quite impossible, since it requires physically non-realistic parameter values. Nevertheless, here again, it is confirmed that the assumed separability of the mixing and elastic free energy terms is to be questioned. The reduced dilation modulus depends upon the nature of the swelling solvent, contrary to the assumption expressed in the swelling theory of Flory–Rehner. These conclusions are similar to those obtained by Eichinger and co-workers[10-14].

The main drawback of the above swelling experiments is that they have been carried out on PDMS networks arising from random crosslinking (γ irradiation), which implies that the molar mass distribution of the elastic chains is broad and that there are many defects in the network topology, such as pendent chains. A second set of swelling experiments has been reported by Brotzman and Eichinger[13] and by Neuburger and Eichinger[14] on PDMS model networks. These tri- and tetrafunctional model networks have been synthesized via endlinking processes by Mark *et al.*[39,40]. For tetrafunctional networks, two methods have been investigated. In the first one, hydroxy-terminated PDMS polymers of known molar mass ($M_c = 18\,500$[13] and $M_c = 26\,000$[14]) are crosslinked by tetraethoxysiloxane, $Si(OEt)_4$. The second endlinking process involves vinyl-terminated PDMS precursors ($M_c = 11\,300$[13] and $M_c = 26\,000$[14]) and 1,3,5,7-tetramethylcyclotetrasiloxane as cyclic crosslinker. In both cases, however, PDMS model networks with elastic chains of equal molar mass ($M_c = 26\,000$[14]) and crosslinkers of different chemical structures exhibit sol-fractions which are rather large (4.7% for the sample crosslinked by $Si(OEt)_4$ and 9.02% for the network in which the cyclic crosslinker is used). These two networks are swollen at 20°C and 30°C, in benzene and in cyclohexane, respectively. It was confirmed that the variation of the reduced dilation modulus, in benzene medium, against λ^2 exhibits a sharp maximum, as expected from molecular theory[28,29]. The existence of the maximum is more questionable when cyclohexane is used as swelling solvent with the same PDMS model network. It is thus confirmed that the reduced dilation moduli are solvent-dependent, regardless of the temperature.

Neuburger and Eichinger[14] have also pointed out that the chemical nature of the crosslinkers may play a role. Therefore, it is assumed that the interaction parameter of the swelling solvent with a given crosslink may be different than what it is with linear chain elements (elastic chains). This difference, which is not taken into account in the Flory–Rehner approach, may also explain the failure of the theory with respect to experiment. Ultimately, it has been found that the experiments carried out in cyclohexane fit rather satisfactorily the 'phantom' network model developed by James and Guth[18-22] and later by Flory[31]. For PDMS model networks swollen in benzene, only qualitative agreement is obtained with respect to the Flory–Erman approach[28,29].

Other types of criticism[41] have been put forward against the Flory–Rehner theory. According to de Gennes[42], the evaluation of the two antagonistic terms in the variation of the total free energy is erroneous. The interaction repulsive energy is largely overestimated. It is not proportional to the square of the polymer concentration because there are large fluctuations in monomer density within a sample. Moreover, the Gaussian hypothesis, used by Flory to calculate the free energy of deformation, does not seem acceptable, since the whole statistics is modified by interactions of excluded volume. In the Flory–Rehner approach, this modification is completely misunderstood. The 'osmotic' contribution to the total free energy is evaluated according to the theories of Flory[5,43] and Huggins[44,45]. The latter are 'mean-field' approaches which ignore the fluctuations in concentration, whereupon the monomer concentration is considered to be uniform. In fact, these statements cannot be applied to a system in which the fluctuations are important and generate, as indicated previously, an overestimation of the free energy. Consequently, the formulation of the Flory–Rehner theory, in its initial form, seems to be questionable. However, according to de Gennes[42], the cancellation of the two above 'errors' (overestimation of the elastic free energy and ignorance of the correlation between segments) can explain the success of the Flory–Rehner approach.

From the above considerations, it appears that none of the existing molecular theories is able to account satisfactorily for the experimental swelling data. This observation may be due to the inadequacy of these theories at their present level of development[30]. Moreover, the sophistication of such theoretical models implies generally adjustment of several parameters. For instance, the constrained junction fluctuation model, introduced by Flory and Erman[28,29], is a rather complicated method of analysing the swelling behaviour of polymer networks. This approach includes three new parameters which are not easy to handle. The first parameter is the 'cycle rank' $\xi = \nu - \mu$, where ν and μ are the concentrations of the elastically effective chains and the effective crosslinks, respectively. To determine ν and μ, the use of branching theories (e.g. the Millar–Macosko theory[46,47]) is necessary, as has been done by Gnanou, Hild and Rempp on poly(ethylene oxide) model networks[48]. The second factor κ measures the severity of the constraints arising from neighbouring chains on the network junctions. The third parameter ζ, used in the Flory–Erman theory, is believed to reflect possible inhomogeneity and/or irregularity in the network topology.

In the present paper, the Flory–Rehner theory has been used as a starting approach, in spite of the drawbacks mentioned in the Introduction. Previous equilibrium swelling data on polystyrene and poly(dimethylsiloxane) model networks have been reanalysed using the contribution of the affine model and the 'phantom' network model. It will be shown that the basic equation of Flory–Rehner can be modified yielding, ultimately, a more satisfactory agreement between experiment and theory.

SOME BASIC CONSIDERATIONS

When a crosslinked polymer network, prepared in the melt, is placed in an excess of an adequate solvent of its elastic chains, it undergoes large deformations induced by swelling, without dissolving. From a practical point of view, to evaluate the equilibrium volume swelling degree Q of a network swollen in a 'good' solvent (i.e., the reciprocal of the equilibrium volume swelling concentration, v), the variation of the total free energy of the binary system has to be calculated. The difference between the chemical potential of the solvent μ_1 inside the pores of the network and that μ_0 in the surrounding pure solvent comprises two terms. The first one, referred to as the 'dilution' (or mixing) term, takes account of the thermodynamic interaction parameter χ between the swelling solvent and the elastically effective chains. The second term corresponds to the tridimensional elastic deformation of the network. As indicated in the Introduction, these two contributions have been calculated separately by Flory and Rehner[3] and can be formulated as

$$\mu_1 - \mu_0$$

$$= RT[\ln(1-v) + v + \chi v^2] \qquad + RT\nu_e\bar{V}\left(v^{1/3} - \frac{2}{f}v\right) \quad (5)$$

('dilution' term) (elastic deformation term)

In equation (5), $\bar{V}$ is the molar volume of the solvent, f is the functionality of the crosslinks and $v = 1/Q$ is the volume fraction of the polymer at equilibrium. At equilibrium swelling, the chemical potential of the solvent is identical inside and outside the swollen network, leading to

$$\mu_1 - \mu_0 = 0 \qquad (6)$$

whereupon the value of the number of elastic chains ν_e per unit volume of dry network is accessible:

$$\nu_e = \frac{\ln(1-v) + v + \chi v^2}{\bar{V}\left(-v^{1/3} + \frac{2}{f}v\right)} \qquad (7)$$

Using this basic equation, semi-quantitative interpretations of many experimental data have been performed with some success. In fact, in the Flory–Rehner treatment[5], two main simplifications have been considered. The logarithmic term $\ln(1-v)$ of equation (7) is developed to the second order. The value of $v^{1/3}$ is considered to be much larger than $(2/f)v$ for networks exhibiting Q values equal to or higher than 10 (which is generally the case for the model networks investigated in the present paper). Under these conditions, equation (7) can be written as

$$\nu_e = \left(\frac{1}{2} - \chi\right)\frac{1}{\bar{V}}Q^{-5/3} \qquad (8)$$

This approximation is valid for networks synthesized in the melt. If the crosslinking process is performed in solution, at a polymer concentration v_c upon crosslinking, equation (8) becomes

$$\nu_e = \left(\frac{1}{2} - \chi\right)\frac{1}{\bar{V}}Q^{-5/3}v_c^{-2/3} \qquad (9)$$

As far as model networks are concerned, it can reasonably be assumed that the number of elastic chains ν_e is related to the molar mass M of the elastic chains by the relation:

$$\nu_c = \frac{1}{M\bar{v}_0} \qquad (10)$$

$\bar{v}_0$ being the specific volume of the dry gel. Using equations (9) and (10), the value of Q can be expressed as

$$Q = \left(\frac{1}{2} - \chi\right)^{3/5}\left(\frac{\bar{v}_0}{\bar{V}}\right)^{3/5} v_c^{-2/5}M^{3/5} \qquad (11)$$

A more general treatment has been proposed by Dusek and Prins[49] in which ν_e is expressed as

$$\nu_e = \frac{\ln(1-v) + v + \chi v^2}{\bar{V}(Bv - Ah_3^{2/3}v^{1/3})} \qquad (12)$$

instead of equation (7). The new parameter h_3, referred to as the 'memory term', characterizes the segment concentration of the chains of the 'relaxation' state. It is related to the concentration v_c at which crosslinking took place:

$$h_3^{2/3} = \frac{\overline{r_c^2}}{\overline{r_{os}^2}} . v_c^{2/3} \tag{13}$$

where $\overline{r_c^2}$ is the mean-square end-to-end distance of the elastic chains in the swollen reference state and $\overline{r_{os}^2}$ is the mean-square end-to-end distance of the corresponding uncrosslinked chains (free chains) of the same length as the elastic chains, at a concentration equivalent to the reference state. From small-angle neutron scattering experiments, performed on polystyrene model networks exhibiting 'labelled' crosslinks, it has been established[50,51] that the ratio $\overline{r_c^2}/\overline{r_{os}^2}$ is close to unity, yielding obviously

$$h_3 = v_c \tag{14}$$

Developing the logarithmic term of equation (12) to the second order, we obtain:

$$\nu_e = \frac{\left(\frac{1}{2} - \chi\right) v^2}{\overline{V}(A v_c^{2/3} v^{1/3} - Bv)} \tag{15}$$

In the affine model developed by Flory[5], the two constants A and B are given by[15]

$$A = 1 \qquad B = \frac{2}{f} \tag{16}$$

Let us now consider the 'phantom' network model, first introduced by James and Guth[18–22]. In this model, the elastically effective chains are considered as 'immaterial' and can cross each other freely without destroying the network topology. They merely transmit the forces exerted on the crosslinks to which they are linked. In the treatment of James and Guth, the value of the constant B is believed to be zero in any case, whereas the value of A may be equal to 1/2. Development of the phantom theory has been achieved by Duiser and Staverman[52], and later by Graessley[53,54]. The constant A has been evaluated by an indirect method from the properties of an ensemble of simple networks referred to as 'micronetworks', comprising a limited number of elastic chains and junction points. According to the calculations of Graessley[53], the value of A depends only upon the functionality f of the crosslinks and is expressed as

$$A = \frac{f-2}{f} \tag{17}$$

Obviously, for the trifunctional networks $A = 1/3$, whereas for tetrafunctional networks $A = 1/2$, which is in agreement with the A value of James and Guth[18–22] and that obtained by Eichinger[55] for 'perfect' networks. As the average functionality f increases, the value of A tends towards 1, which corresponds to that determined in the classical theory of Flory and Wall[15]. The new version of the theory of Flory[31,56] takes into account the above contributions of James and Guth, of Duiser and Staverman and of Graessley.

By using the A and B values derived from the phantom theory, equation (15) can be written as

$$\nu_e = \frac{\left(\frac{1}{2} - \chi\right) v^{5/3}}{\overline{V}\left(\frac{f-2}{f}\right) v_c^{2/3}} \tag{18}$$

Introducing into equation (18) the equilibrium volume swelling degree $Q = v^{-1}$ and assuming ideality of the network (equation (10)), we obtain finally

$$Q = \left(\frac{1}{2} - \chi\right)^{3/5} \left(\frac{\bar{v}_0}{\overline{V}}\right)^{3/5} \left(\frac{1}{v_c}\right)^{2/5} \left(\frac{f}{f-2}\right)^{3/5} M^{3/5} \tag{19}$$

In this relation, the equilibrium volume swelling degree Q is related to the parameters which are experimentally accessible for a model network arising from an endlinking process: the volume segment concentration upon crosslinking v_c, the functionality of the crosslinks f and the average molar mass of the elastic chains M.

EXPERIMENTAL

Synthesis of model networks by endlinking processes

Synthesis of polystyrene model networks. It is well known that anionic 'living' polymerization carried out at low temperature, in an aprotic solvent, under argon atmosphere or high vacuum, using bifunctional organometallic initiators, yields polymers exhibiting a known average molar mass and a narrow mass distribution[57]. These well-defined living bifunctional polymers serve as polymeric 'precursors' in endlinking processes, leading to the formation of model networks.

The synthesis of bifunctional living polystyrene, fitted at both chain ends with organic sites, requires the use of bifunctional initiators such as bisodium α-methylstyrene 'tetramer' or potassium naphtylide. These carbanionic

Table 1 Characteristics of polystyrene model networks (swelling solvent : benzene)

Sample	M_{LS}[a]	DVB/LE[b]	v_c[c]	w_s (%)[d]	Q[e]
1791	5300	3	0.091	0.5	8.50
1814	7600	3.3	0.084	0.8	10.20
1790	10600	3	0.091	2.0	12.60
1947	14500	2.8	0.091	2.0	12.93
1977[f]	14700	2.9	0.090	2.1	12.07
1941	19700	3	0.091	3.4	15.84
1789	21300	3	0.084	–	19.10
1872	31500	2.7	0.091	–	24.34
1878	39500	2.9	0.091	3.0	27.80
1876	60000	3	0.100	5.0	37.80
1863	10800	3.2	0.180	–	7.70
1944	19000	3.8	0.180	3.5	10.70
1950	21000	4.2	0.250	5.4	10.90
1945	21500	4.3	0.250	4.1	11.20

[a] Average molar mass of the elastic chains determined by light scattering
[b] Number of divinylbenzene molecules per living end
[c] Volume fraction of polymer chains upon crosslinking
[d] Weight percentage of soluble extractable polystyrene (sol-fraction)
[e] Equilibrium volume swelling degree in benzene
[f] Polystyrene model network prepared model prepared with pure *meta*-DVB isomer

sites, located at both chain ends, are able to initiate the polymerization of a bisunsaturated monomer such as divinylbenzene (DVB), whereupon gelation of the reaction medium takes place. Details of this endlinking process are given in previous papers[58–61]. A crosslinked polystyrene network is formed in which each precursor polymer chain should be connected to two different poly(DVB) nodules. The model network obtained consists of ν linear chain elements (elastic chains) connected by $2\nu/f$ f-functional branch points. If the experimental conditions are chosen adequately, the networks are homogeneous and optically transparent, provided no syneresis has occurred. In such a process, crosslinking takes place without major change of the volume segment concentration v_c upon crosslinking, since it merely involves polymerization of a small amount of DVB as comonomer. Three parameters essentially govern this type of endlinking process: (i) the average molar mass M of the elastic chains (i.e. the average length of polystyrene precursor between two neighbouring poly(DVB) crosslinks); (ii) the overall concentration v_c of the polymer at the gel point (i.e. the volume fraction of polystyrene chains upon crosslinking); and (iii) the number of molecules of bisunsaturated monomer per living end (DVB/LE); *a priori*, if this ratio increases, the average functionality of the crosslinks should increase too.

After extraction of the fraction of soluble polystyrene (i.e. the sol-fraction w_s), the network is placed in an excess of solvent (benzene). Its equilibrium swelling is reached after several days and thus the equilibrium swelling Q can be determined.

Synthesis of poly(dimethylsiloxane) model networks. A chemical reaction on polymer chains is another method of obtaining crosslinked networks. It is well

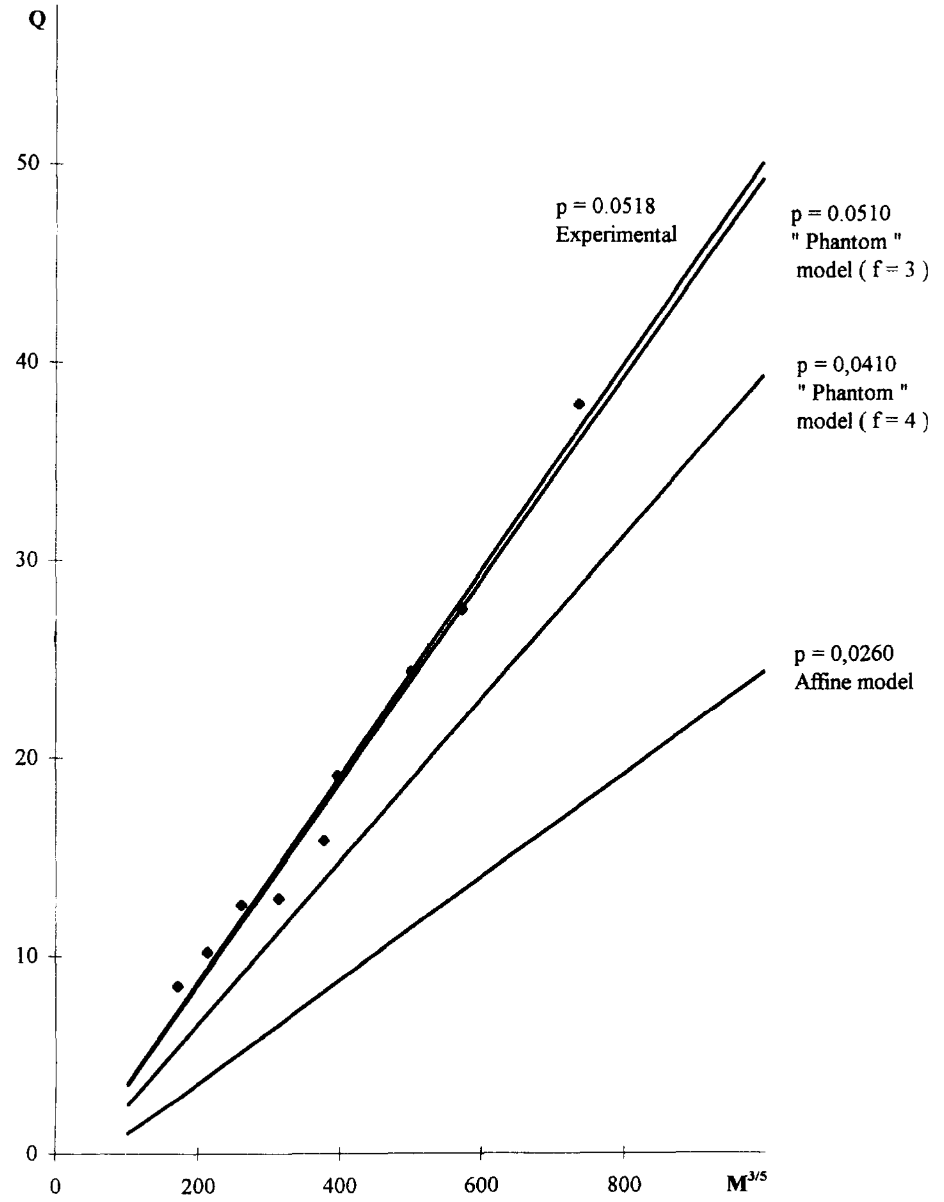
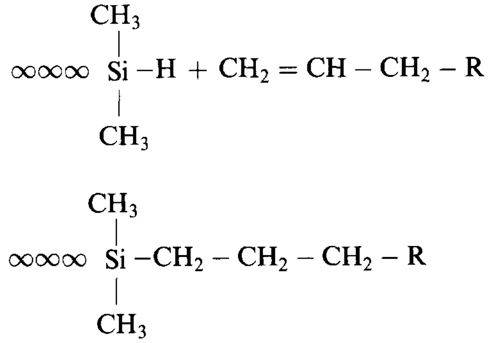


Figure 1 Variation of equilibrium volume swelling degree Q in benzene as a function of $M^{3/5}$, for the polystyrene model networks. Experimental: slope = 0.0518; affine model: slope = 0.0260; 'phantom' model: slope = 0.0510 (f = 3), slope = 0.0410 (f = 4). The accuracy of the determination of the equilibrium volume swelling concentration is about 3%, whereas the accuracy of the determination of the average molar mass M of elastic chains by light scattering is about 5%

known[62] that the Si–H functions are able to yield addition reactions with unsaturated vinylic or allylic compounds:



$$\text{∞∞∞}\ \mathrm{Si(CH_3)_2{-}H + CH_2{=}CH{-}CH_2{-}R}$$

$$\text{∞∞∞}\ \mathrm{Si(CH_3)_2{-}CH_2{-}CH_2{-}CH_2{-}R}$$

This hydrosilysation reaction has been applied, by Herz and co-workers[60,63,64], to the synthesis of model networks by endlinking processes. For this purpose, α,ω-functional poly(dimethylsiloxane) (PDMS), fitted at both chain ends with Si–H functions, has been reacted with selected plurifunctional allyloxy compounds in the presence of chloroplatinic acid as catalyst. In this experiment, triallyloxy-1,2,3 propane or tris (allyloxy)-1,3,5 triazine ($f = 3$), tetraallyloxyethane ($f = 4$) and bis-allyloxy-3-dimethyl allyloxy-2,2 propane oxide ($f = 6$) have been chosen as functional allyloxy reactives. Exact stoichiometry and efficient stirring are required to obtain homogeneous, well-defined model networks. These reactions are carried out either in bulk or in the presence of a good solvent of PDMS chains, such as heptane. Gelation of the reaction medium takes place readily and the model networks obtained exhibit PDMS elastic chains connected at their two ends with f-functional crosslinks. In this endlinking process, both the average molar mass M of the elastic chains between crosslinks and the functionality f are known, and should remain constant throughout a given sample.

Prolonged solvent extraction (Soxhlet) has been performed on the networks obtained, yielding rather low amounts of extractable polymer, even if the linear PDMS precursor may well contain some cyclic homologues, which obviously cannot participate in the crosslinking reaction. Ultimately, the model networks are swollen to equilibrium, either in heptane or in toluene.

Swelling equilibrium measurements

The determination of the equilibrium volume swelling degree Q of a network has been carried out using traditional gravimetric swelling experiments, as shown elsewhere[58]. The equilibrium weight swelling degree G of a network is defined as the ratio of its weight in the swollen state to its weight in the dry state. It can be determined experimentally with satisfactory accuracy (about 3%). At least three measurements of G were carried out, using small cubes of swollen gel of different weight and sampled at different locations in a given gel. The value of Q can be calculated by the relation

$$Q = 1 - (G - 1)\frac{\bar{v}_s}{\bar{v}_g} \qquad (20)$$

$\bar{v}_s$ and $\bar{v}_g$ being the specific volumes of the solvent and network, respectively.

RESULTS AND DISCUSSION

Variation of equilibrium volume swelling degree with molar mass of the elastic chains

Polystyrene model networks. A series of polystyrene model networks has been synthesized by an endlinking process, the volume fraction v_c of the polymer upon crosslinking remaining quasi-constant ($v_c = 0.09$). The mole ratio of DVB to living end (DVB/LE) was generally located between 2.7 and 3.3 (say 3 on average)[4]. The data obtained are summarized in *Table 1*. In these experiments (samples 1791 to 1876) the molar ratio of styrene to initiator varies extensively, the domain of molar mass M of the polystyrene precursors extending from 5000 to 60 000 (values of M being determined by light scattering).

Table 2 Determination of the interaction parameter for the benzene–polystyrene model network from equilibrium swelling experiments, using the affine model

Sample	M_{LS}[a]	Q[b]	Second term of equation (23)	First term of equation (23) $f = 3$	First term of equation (23) $f = 4$	First term of equation (23) $f = 6$	χ[c] $f = 3$	χ[c] $f = 4$[e]	χ[c] $f = 6$	$v = Q^{-1}$[d]
1791	5 300	8.50	0.5420	−0.0255	−0.0556	−0.0757	0.5165	0.4914	0.4663	0.1176
1814	7 600	10.20	0.5352	−0.0349	−0.0559	−0.0764	0.5003	0.4793	0.4583	0.0980
1790	10 600	12.60	0.5281	−0.0450	−0.0665	−0.0841	0.4831	0.4617	0.4400	0.0793
1947	14 500	12.93[g]	0.5273	−0.0367	−0.0506	−0.0645	0.4906	0.4767	0.4628	0.0773
1977[f]	14 700	(12.07)	(0.5294)	(−0.0300)	(−0.0428)	(−0.0557)	(0.4994)	(0.4866)	(0.4737)	(0.0828)
1941	19 700	15.84[g]	0.5221	−0.0451	−0.0578	−0.0704	0.4769	0.4643	0.4517	0.0631
1789	21 300	19.10	0.5181	−0.0646	−0.0786	−0.0926	0.4535	0.4395	0.4255	0.0523
1872	31 500	24.34	0.5141	−0.0739	−0.0860	−0.0981	0.4402	0.4281	0.4160	0.0410
1878	39 500	27.80	0.5123	−0.0776	−0.0886	−0.0997	0.4347	0.4237	0.4126	0.0359
1876	60 000	37.80	0.5089	−0.0943	−0.1041	−0.1140	0.4146	0.4048	0.3949	0.0264

[a] Average molar mass of elastic chains determined by light scattering
[b] Equilibrium volume swelling degree
[c] Interaction parameter for benzene–polystyrene model network for functionalities f equal to 3, 4 and 6, respectively
[d] Equilibrium volume swelling concentration
[e] The values of χ for $f = 4$ have been already calculated in previous papers[4,72]
[f] Sample prepared with pure *meta*-DVB isomer
[g] Underestimated values of Q

The sol-fraction w_s (i.e. the amount of extractable polystyrene not incorporated into the network) increases slowly with increasing molar mass M. Obviously, the number of living sites decreases with increasing length of the elastic chains, whereupon the amount of free polystyrene chains becomes larger.

The equilibrium volume swelling degree Q, measured in benzene as swelling solvent, increases with increasing molar mass of the precursor chains. This result is interesting, since it confirms that the pore size (mesh size) of the network is indeed a function of the molar mass of the polystyrene precursor. The length of the elastic chains determines the porosity of the network (i.e. its equilibrium swelling degree).

In samples 1863 to 1945 of *Table 1*, the values of the volume fraction v_c at which crosslinking takes place are higher (0.18 and 0.25) and the DVB/LE mole ratio is also higher (3.2 to 4.3). It can be observed that v_c plays no major role as far as the Q value is concerned, even though a slight decrease in Q can be evidenced when v_c increases from 0.09 to 0.25 for a given value of M.

To test the validity of the equilibrium swelling equations, the first series of model networks (samples 1791 to 1876 of *Table 1*) has been used. *Figure 1* shows the variation in the equilibrium swelling degree Q as a function of $M^{3/5}$. As expected from equation (11) (affine model) and equation (19) ('phantom' model), a straight line is obtained, provided the molar mass of the elastic chains does not exceed 60 000[65]. A comparison between the slope of this line and those arising from the equilibrium swelling equations should determine which of the two models (if any) is able to account for the experimental data. The experimental slope $p_{\exp}$ determined in *Figure 1* is $p_{\exp} = 0.0518$. To calculate the theoretical slopes, the following values have been introduced in equations (11) and (19): $\overline{V} = 89.14$ ml is the molar volume of the swelling solvent (benzene), $\overline{v}_0 = 0.95\,\mathrm{ml\,g^{-1}}$ is the specific volume of the dry polystyrene network, $v_c = 0.09$ is the volume fraction upon crosslinking, and $(1/2 - \chi) = 0.0442$ is the value of the interaction parameter χ obtained by Dondos and Benoit[66] for the binary system benzene–linear poly-

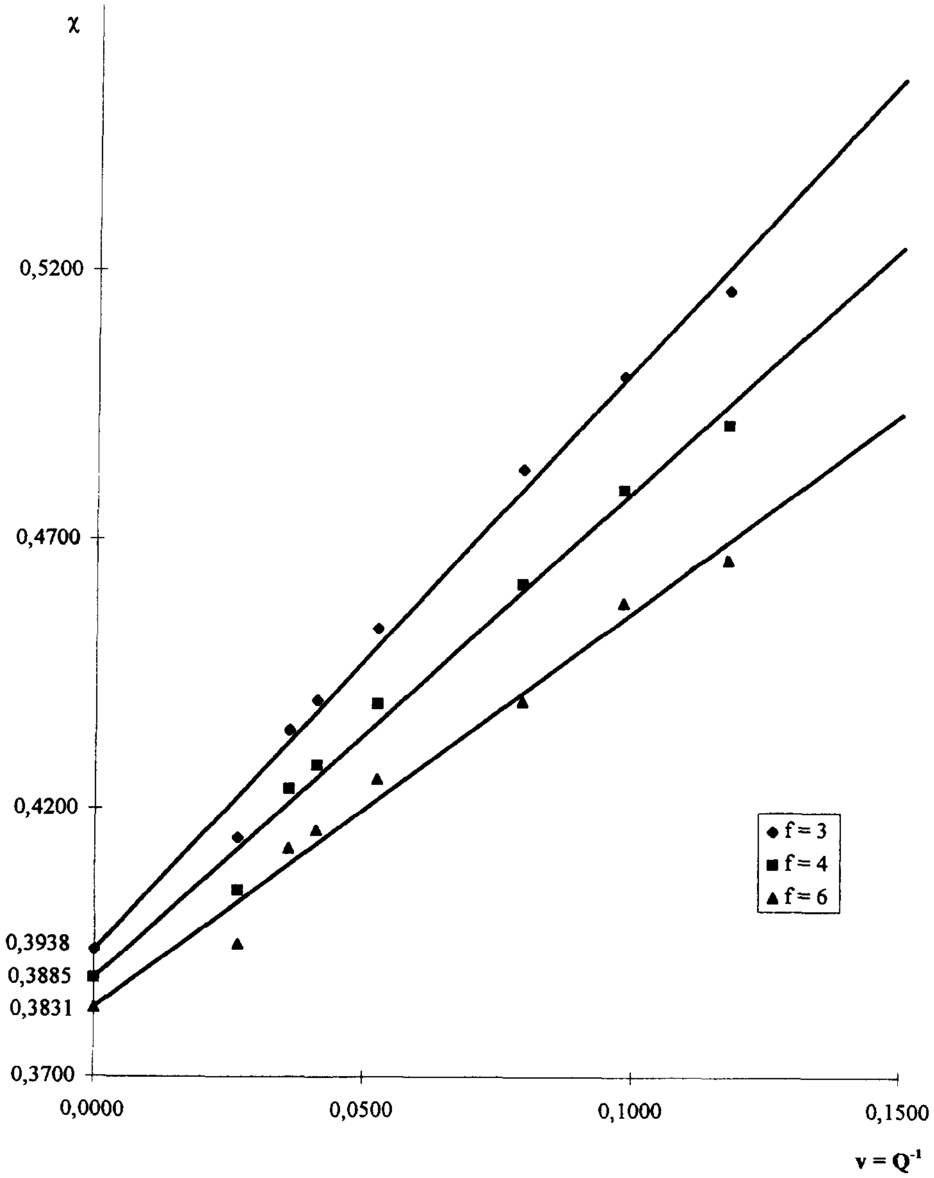


Figure 2 Variation of interaction parameter χ for the benzene–polystyrene model network as a function of equilibrium volume swelling concentration $\nu = Q^{-1}$, for the affine model. For ◆◆◆ $f = 3$, $\chi_0 = 0.3938$; for ■■■ $f = 4$, $\chi_0 = 0.3885$; for ▲▲▲ $f = 6$, $\chi_0 = 0.3831$

styrene. According to the Flory–Rehner relation (equation (11)), the theoretical slope p_{aff} is given by

$$p_{\mathrm{aff}} = \left(\frac{1}{2} - \chi\right)^{3/5} \left(\frac{\bar{v}_0}{\bar{V}}\right)^{3/5} v_c^{-2/5} = 0.0260$$

The p_{aff} value obtained does not match the experimental value ($p_{\mathrm{exp}} = 0.0518$). On the other hand, according to the phantom model (equation (19)), the theoretical slope p_{ph} is expressed by

$$p_{\mathrm{ph}} = \left(\frac{1}{2} - \chi\right)^{3/5} \left(\frac{\bar{v}_0}{\bar{V}}\right)^{3/5} v_c^{-2/5} \left(\frac{f-2}{f}\right)^{3/5}$$

yielding

$$p_{1\mathrm{ph}} = 0.0510 \qquad \text{for } f = 3$$

and

$$p_{2\mathrm{ph}} = 0.0410 \qquad \text{for } f = 4$$

The experimental slope ($p_{\mathrm{exp}} = 0.0518$) is practically identical to $p_{1\mathrm{ph}}$. These results strongly support the phantom network model. Consequently, a value of f of the order of 3 (or 4) is plausible, provided the polystyrene model networks have been prepared with a molar ratio DVB/LE of about 3. Should this ratio be higher, an increase of the functionality f of the crosslinks should be expected.

If the length of the elastic chains M increases beyond 60 000, it is observed that the corresponding experimental points are systematically below the straight line[65]. For these networks, the proportions of extractable polystyrene (about 10%) cannot be neglected and consequently the number of defects (pendant chains, loops, trapped entanglements etc.) becomes larger and the criterion of ideality of the networks (equation (10)) is no longer valid. This may explain the difference between the Q values observed and those expected.

A more elaborate treatment has been put forward to obtain the Flory–Huggins interaction parameter χ between the swelling solvent and the elastic chains of the network as a function of the equilibrium volume swelling degree Q. It originates from the general expression of the equilibrium swelling of model networks in a 'good' solvent, given below:

$$\frac{1}{M\bar{v}_0} = \frac{\ln(1 - Q^{-1}) + Q^{-1} + \chi Q^{-2}}{\bar{V}(Bv - A v_c^{2/3} Q^{-1/3})} \tag{21}$$

In equation (21), the molar volume $\bar{V}$ and the solvent–network interaction parameter χ are the two coefficients characterizing the swelling solvent. The values of χ for polystyrene model networks swollen to equilibrium in benzene can be calculated, knowing the values Q and M, by the relation

$$\chi = \frac{\bar{V}}{\bar{v}_0}\frac{1}{M}(BQ - A v_c^{2/3} Q^{5/3}) - [Q + Q^2 \ln(1 - Q^{-1})] \tag{22}$$

The second term of equation (22) depends only upon Q; it is always negative and much larger than the first term, which depends upon M, v_c, f and Q. The affine model, with $A = 1$ and $B = 2/f$ (equation (16)), yields

$$\chi = \frac{\bar{V}}{\bar{v}_0}\frac{1}{M}\left(\frac{2}{f}Q - v_c^{2/3} Q^{5/3}\right) - [Q + Q^2 \ln(1 - Q^{-1})] \tag{23}$$

The use of the phantom model implies that $A = (f-2)/f$ (equation (17)) and $B = 0$, and the χ values are expressed as

$$\chi = -\left(\frac{f-2}{f}\right)\frac{\bar{V}}{\bar{v}_0}\frac{1}{M} v_c^{2/3} Q^{5/3} - [Q + Q^2 \ln(1 - Q^{-1})] \tag{24}$$

Values of χ have been calculated using equations (23) and (24), assuming the functionality f of the crosslinks to be equal to 3, 4 or 6.

The data, as treated by the affine model (equation (23)), are displayed in *Table 2* and *Figure 2*. The variation of χ is plotted as a function of the reciprocal of the

Table 3 Determination of the interaction parameter for the benzene–polystyrene model network from equilibrium swelling experiments, using the 'phantom' model

				First term of equation (24)			χ^c			
Sample	$M_{\mathrm{LS}}{}^a$	Q^b	Second term of equation (24)	$f = 3$	$f = 4$	$f = 6$	$f = 3$	$f = 4^e$	$f = 6$	$v = Q^{-1\,d}$
1791	5 300	8.50	0.5420	−0.0419	−0.0629	−0.0838	0.5001	0.4791	0.4582	0.1176
1814	7 600	10.20	0.5352	−0.0396	−0.0594	−0.0792	0.4956	0.4758	0.4560	0.0980
1790	10 600	12.60	0.5281	−0.0404	−0.0606	−0.0808	0.4877	0.4675	0.4473	0.0793
1947	14 500	12.93^f	0.5273	−0.0308	−0.0462	−0.0616	0.4965	0.4811	0.4657	0.0773
1977^e	14 700	(12.07)	(0.5294)	(−0.0271)	(−0.0407)	(−0.0542)	(0.5023)	(0.4887)	(0.4752)	(0.0828)
1941	19 700	15.84^f	0.5221	−0.0318	−0.0477	−0.0636	0.4903	0.4744	0.4595	0.0631
1789	21 300	19.10	0.5181	−0.0402	−0.0603	−0.0804	0.4779	0.4578	0.4377	0.0523
1872	31 500	24.34	0.5141	−0.0407	−0.0611	−0.0814	0.4734	0.4530	0.4327	0.0410
1878	39 500	27.80	0.5123	−0.0405	−0.0608	−0.0810	0.4718	0.4515	0.4313	0.0359
1876	60 000	37.80	0.5089	−0.0445	−0.0668	−0.0890	0.4644	0.4421	0.4199	0.0264

[a] Average molar mass of elastic chains determined by light scattering
[b] Equilibrium volume swelling degree
[c] Interaction parameter for benzene–polystyrene model network for functionalities f equal to 3, 4 and 6, respectively
[d] Equilibrium volume swelling concentration
[e] Sample prepared with pure *meta*-DVB isomer
[f] Underestimated values of Q

equilibrium swelling (volume fraction) $v = Q^{-1}$ for these three values of f. In each case, the variation of χ with respect to v has been found to be linear. The slope of the straight lines and the extrapolated values of χ at $v = 0$, which should be the interaction parameter χ_0 of the benzene–linear polystyrene system, are calculated by the least-square method. Let us recall that the value of χ_0, determined independently, is known to be 0.456[66]. It must be noted that three networks of *Table 2* (samples 1947, 1977 and 1941) are not included in this calculation for the following reasons. The choice of the DVB isomer as crosslinking agent affects appreciably the swelling behaviour of networks exhibiting elastic chains of the same length. Samples 1947 and 1977, which differ only in the nature of the DVB used (*para-* and *meta-*DVB mixture or pure *meta-*DVB, respectively), exhibit different equilibrium volume swelling degrees Q (by about 8%), confirming previous results obtained on polystyrene networks prepared by free radical copolymerization with different DVB isomers[67,68]. Therefore, sample 1977 of *Table 2* (prepared with pure *meta-*DVB) is not taken into account for the least-square calculation in *Figure 2*. On the other hand, the Q values of networks 1947 ($Q = 12.93$) and 1941 ($Q = 15.84$) are probably underestimated, leading to an overestimation of the first term of equation (23) (see *Table 2*) and consequently to values of χ which are too large. That is why the swelling behaviour of these two networks has not been taken into account in the least-square calculation. The interaction parameter χ was shown to decrease with increasing values of Q, according to a relation of the form

$$\chi = \chi_0 + aQ^{-1} \qquad (25)$$

Thus, the Flory–Huggins interaction parameter may not be identical for the systems solvent–linear polymer and solvent–network ($\chi = \chi_0$). The dependence of the interaction parameter on the equilibrium swelling

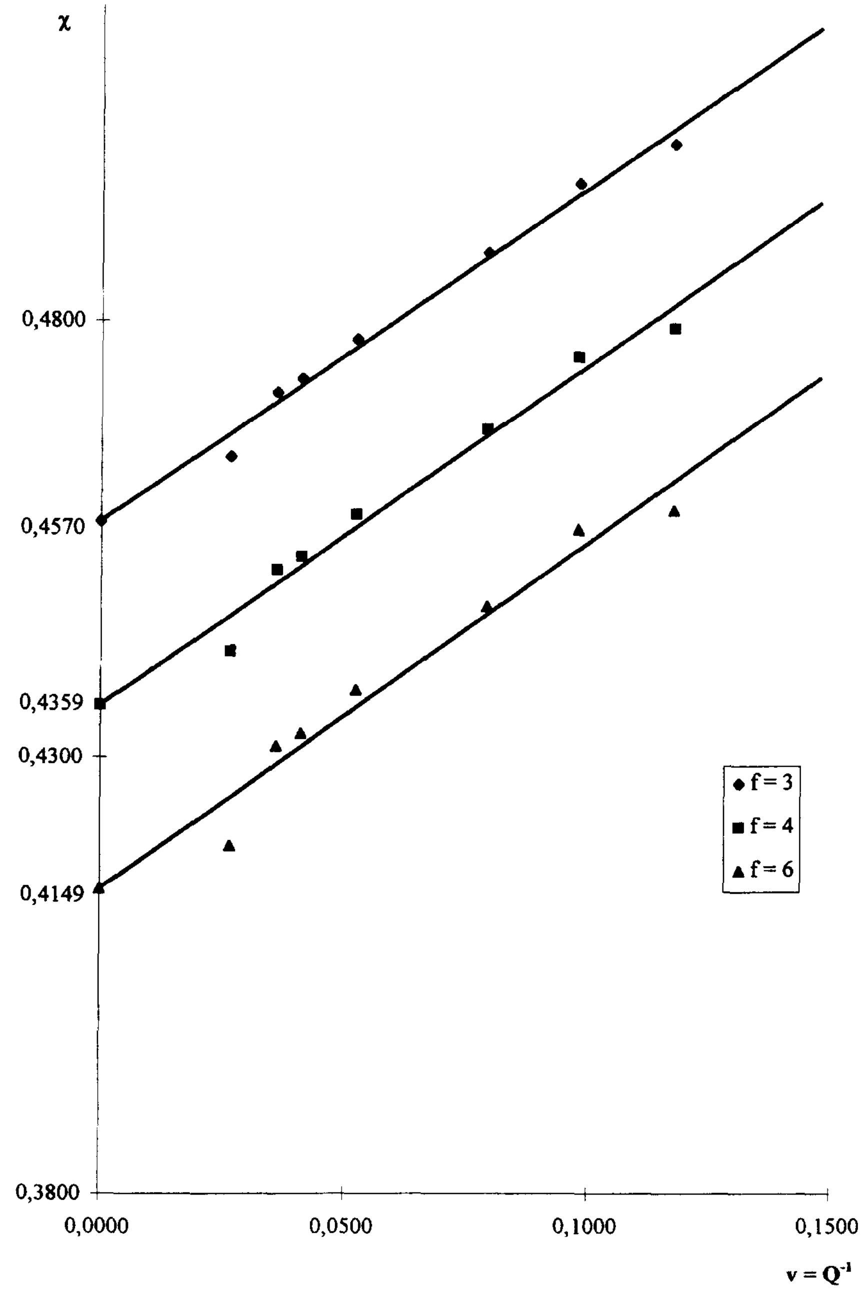


Figure 3 Variation of interaction parameter χ for the benzene–polystyrene model network as a function of equilibrium volume swelling concentration $\nu = Q^{-1}$, for the 'phantom' model. For ◆◆◆ $f = 3$, $\chi_0 = 0.4570$; for ■■■ $f = 4$, $\chi_0 = 0.4359$; for ▲▲▲ $f = 6$, $\chi_0 = 0.4149$

concentration is not surprising. Experiments carried out by Candau *et al.*[69,70] on model polymers with branched structure ('comb' and 'star' polymers) similarly yield a linear dependence of χ on the polymer concentration v. For the three functionalities considered, the calculation of the slope of the straight lines leads to $a = 1.078$ ($f = 3$), $a = 0.906$ ($f = 4$) and $a = 0.735$ ($f = 6$). The corresponding values of χ_0 at $v = 0$ are $\chi_0 = 0.3938$ ($f = 3$), $\chi_0 = 0.3885$ ($f = 4$) and $\chi_0 = 0.3831$ ($f = 6$). These data indicate that χ_0 decreases as the functionality of the crosslinks increases. However, the values obtained are far from that expected ($\chi_0 = 0.456$). Consequently, the affine model is not able to account for the experimental data on polystyrene model networks swollen to equilibrium in benzene.

A similar calculation has been carried out using the phantom model (equation (24)). The data obtained are summarized in *Table 3* and *Figure 3*. As previously, and for the same reasons, the three networks (samples 1947, 1977 and 1941) are not influenced by the least-square calculation. Here again, and for the three functionalities, straight lines are obtained for the variation of χ with respect to Q^{-1} expressed by equation (25). In this case, the slopes of the lines are quasi-identical: $a = 0.387$ ($f = 3$), $a = 0.388$ ($f = 4$) and $a = 0.396$ ($f = 6$). The determination of the values of χ_0 yields $\chi_0 = 0.4570$ ($f = 3$), $\chi_0 = 0.4359$ ($f = 4$) and $\chi_0 = 0.4149$ ($f = 6$). These results are quite satisfactory for $f = 3$ and even for $f = 4$, the expected value of χ_0 for the binary system benzene–linear polystyrene being 0.456. Contrary to the affine model, the phantom theory precisely accounts for the experimental swelling experiments. It is thus confirmed that the average functionality of the poly(DVB) nodules is located between 3 and 4 (probably closer to 3), provided the mole ratio of DVB to living end remains near 3. Obviously, additional experiments should be performed with higher amounts of DVB per living end (the other parameters M and v_c remaining identical). In these conditions, one can reasonably expect an increase in functionality.

Poly(dimethylsiloxane) model networks. A similar treatment has been carried out on poly(dimethylsiloxane) model networks. A series of PDMS networks has been prepared, using tetraallyloxyethane ($f = 4$) as crosslinking agent, under standard conditions. The polymer volume fraction v_c upon crosslinking was kept constant ($v_c = 0.67$), the solvent used was toluene and the average molar mass of the PDMS precursors, determined by light scattering, was extended from 1000 to 17 500, as shown in *Table 4*. All the gels obtained have been submitted to extraction (Sohxlet) with toluene over 48 h. The resulting sol-fraction is rather large and reaches 9% for the highest molar mass of the PDMS precursor ($M = 17\,500$). The extracted gels have been swollen to equilibrium in an excess of toluene. To a first approximation, it can be assumed that toluene is a theta-solvent for PDMS chains. For this reason, and due to the fact that the polymer concentration v_c at the gel point is very high ($v_c = 0.67$), the equilibrium volume swelling degree remains low ($3 < Q < 8$). As expected, it is observed that Q increases with respect to the molar mass M of the elastic chains.

Table 4 Characteristics of poly(dimethylsiloxane) model networks (swelling solvent: toluene). The crosslinking agent is tetrallyloxyethane ($f = 4$)

M_{LS}[a]	ν_c[b]	ω_s %[c]	Q[d]
1 000	0.67	3.3	3.13
1 700	0.67	6	3.86
2 300	0.67	4	4.21
3 800	0.67	4	5.12
7 100	0.67	4	5.66
17 500	0.67	9	8.25

[a] Average molar mass of PDMS chains determined by light scattering
[b] Volume fraction of polymer chains upon crosslinking
[c] Weight percentage of soluble extractable poly(dimethylsiloxane) (sol-fraction)
[d] Equilibrium volume swelling degree in toluene

In *Figure 4*, it is found experimentally that Q is a function of $M^{3/8}$ (instead of $M^{3/5}$ in a 'good' swelling solvent), the slope of the straight line obtained being $p_{\text{exp}} = 0.1912$. To account for these data, the logarithmic term $\ln(1 - Q^{-1})$ of the general swelling equation for model networks (equation (21)) has to be developed to the third order, leading to

$$\frac{1}{M\overline{v}_0} = \frac{\left(\frac{1}{2} - \chi\right)Q^{-2} + \frac{Q^{-3}}{3}}{\overline{V}(Av_c^{2/3}Q^{-2/3} - BQ^{-1})} \tag{26}$$

Equation (26) can be rearranged as

$$Q = \left(\frac{\overline{v}_0}{\overline{V}}\right)^{3/8}\left[\frac{(\frac{1}{2} - \chi)Q + \frac{1}{3}}{Av_c^{2/3} - BQ^{-2/3}}\right]^{3/8} M^{3/8} \tag{27}$$

If the phantom model is used to interpret the swelling experiments, the two constants A and B are expressed as $A = (f - 2)/f$ which involves $A = 1/2$ (since the PDMS model networks have been prepared with a tetrafunctional reactive as crosslinker), and by $B = 0$. Since the networks are swollen to equilibrium in toluene (a theta-solvent of PDMS chains), one can assume that $(1/2 - \chi)$ tends towards 0. Equation (27) can thus be expressed as

$$Q = \left(\frac{\overline{v}_0}{\overline{V}}\right)^{3/8}\left(\frac{1}{3}\right)^{3/8}\left(\frac{f}{f-2}\right)^{3/8} v_c^{-1/4} M^{3/8} \tag{28}$$

For the system considered, the specific volume of the dry gel $\overline{v}_0 = 1.024\,\text{ml}\,\text{g}^{-1}$, the molar volume of toluene is $\overline{V} = 106.27\,\text{ml}$, the constant A is 1/2 (i.e. $f/(f - 2) = 2$), and the volume fraction at which crosslinking takes place is constant: $v_c = 0.67$. Using these parameters, the theoretical slope of the plot of Q against $M^{3/8}$ is $p_{\text{ph}} = 0.1664$, whereas the experimental slope is $p_{\text{exp}} = 0.1917$. As shown in *Figure 4*, the agreement between experiment and the phantom model cannot be considered completely satisfactory.

Other experiments have been performed using PDMS precursors and tetraallyloxyethane as crosslinker. In that case, after extraction of the soluble PDMS, the model networks obtained have been swollen to equilibrium in a 'good' solvent of polymer chains, such as heptane, instead of a theta-solvent, such as toluene. The data obtained are summarized in *Table 5*. Since the molar mass domain is similar to that of the samples shown in *Table 4*, one can expect sol-fractions to be located between 4 and 9%. Obviously, the Q values obtained ($5 < Q < 13$) are larger than those arising from the swelling experiments carried out in toluene. Here again, a proportionality law between Q and $M^{3/5}$ is obtained in

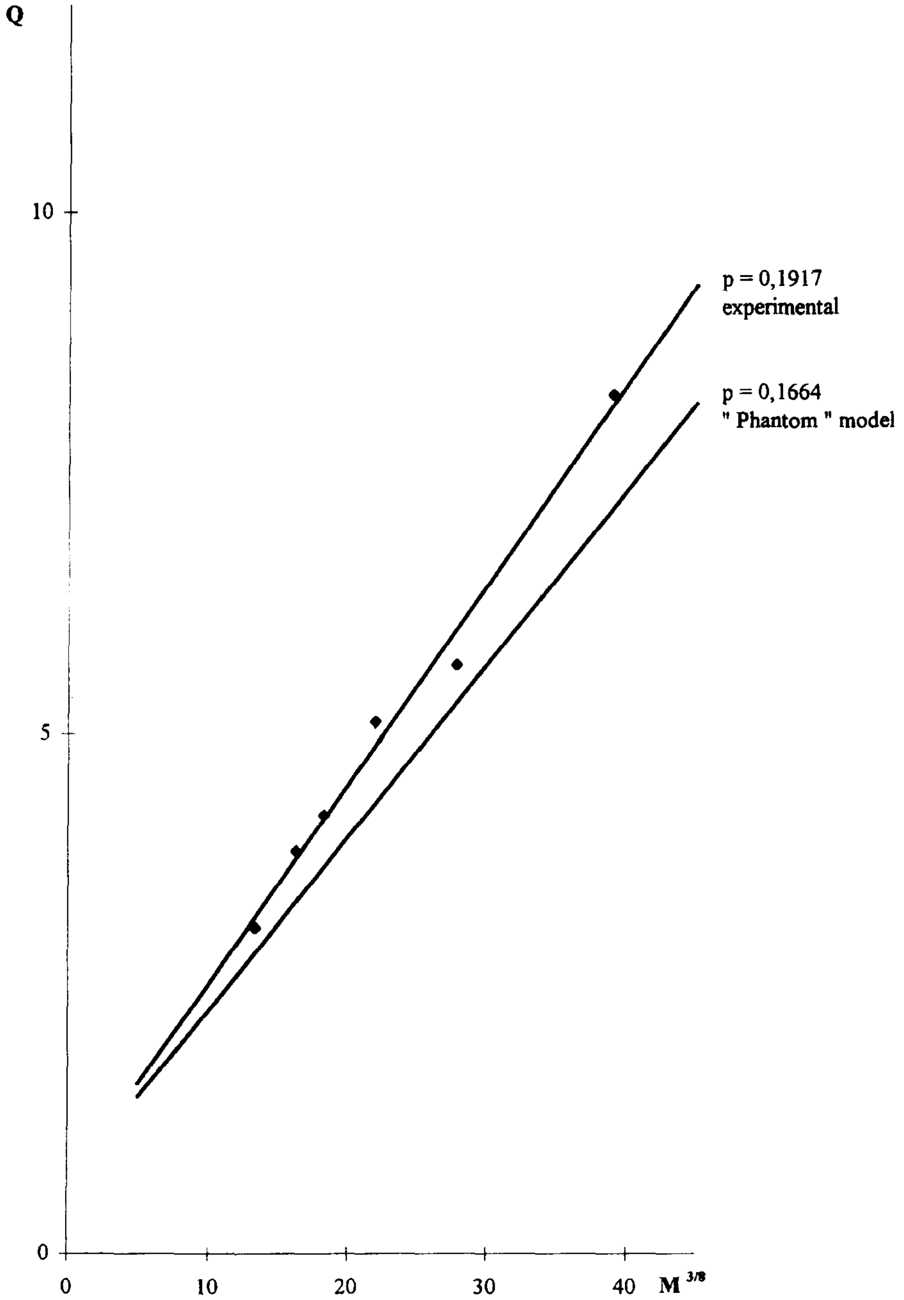


Figure 4 Variation of equilibrium volume swelling degree Q in toluene as a function of $M^{3/8}$ for the poly(dimethylsiloxane) model networks. Experimental: slope = 0.1917; 'phantom' model: slope = 0.1664. The accuracy of the determination of the equilibrium volume swelling concentration is about 3%, whereas the accuracy of the determination of the average molar mass M of elastic chains by light scattering is about 5%

Figure 5, as expected from the predictions of both affine and phantom theories. The experimental slope of the straight line obtained is $p_{\text{exp}} = 0.0374$. To calculate the theoretical slopes, equation (11) (affine model) and equation (12) (phantom model) have been used. For the binary system heptane–PDMS network, the parameters available are: $\bar{v}_0 = 1.024\,\text{ml}\,\text{g}^{-1}$, $\bar{V} = 146.5\,\text{ml}$, $v_c = 0.67$ and $(1/2 - \chi) = 0.111$[71]. The corresponding theoretical slopes for $f = 4$ are $p_{\text{aff}} = 0.0159$ (affine) and $p_{\text{ph}} = 0.0242$ (phantom), as shown in *Figure 5*. Consequently, these data indicate strong departure from the predictions of the two classical models. Neither the affine model nor the phantom model are able to account for the experimental swelling data concerning PDMS networks swollen in a 'good' solvent (heptane). These results may be explained partially by the fact that the networks investigated exhibit rather large amounts of extractable polymers, which implies the existence of defects in the network topology. A second source of error may arise from the uncertainty in the value of $(1/2 - \chi) = 0.111$ for the system PDMS–heptane.

Variation of equilibrium volume swelling degree with nature of the swelling solvent

This study has been carried out on polystyrene model networks synthesized by an endlinking process under standard conditions ($v_c = 0.09$, DVB/LE = 3 and M = 14 500, 14 700 and 31 500, respectively). The values of the equilibrium volume swelling degree Q of the networks have been determined in various swelling solvents (chloroform, benzene, tetrahydrofuran, 1,2-dichloroethane, tetrahydrofurfuryl alcohol and cyclohexane)[72] as shown in *Table 6*. For any given network, the lowest Q values are obtained with tetrahydrofurfuryl alcohol and

Table 5 Characteristics of poly(dimethylsiloxane) model networks (swelling solvent: heptane)

M_{LS}[a]	ν_0[b]	Q[c]
3775	0.67	5.50
4500	0.67	5.90
8700	0.67	9.60
13 250	0.67	11.20
17 100	0.67	13.20

The crosslinking agent is tetrallyloxyethane ($f = 4$)

[a] Average molar masse of the PDMS chains determined by light scattering

[b] Volume fraction of polymer chains upon crosslinking

[c] Equlibrium volume swelling degree in heptane

cyclohexane, the latter being a theta-solvent for linear polystyrene at 34.5°C. The relative variation of Q from one network to another is similar for each of the swelling solvents considered. It is confirmed that the chemical nature of the DVB isomer used in the crosslinking processes influences the values of Q. Sample 1977, which has been prepared with pure *meta*-DVB isomer, systematically exhibits lower Q values than those obtained with sample 1947, synthesized in identical experimental conditions (v_c, M, DVB/LE), but with a *para-meta*-DVB mixture as crosslinker. As expected, the values of Q and M vary in the same way, whatever the swelling solvent may be. However, the influence of the length of the elastic chains M on the equilibrium volume swelling Q is considerably reduced with tetrahydrofurfuryl alcohol and cyclohexane as swelling solvents.

In this study, the values of the solvent–network interaction parameter χ have been calculated for all the swelling solvents, as previously described. From the above data, it has been established that the variation of χ with $v = Q^{-1}$ is linear in the volume swelling

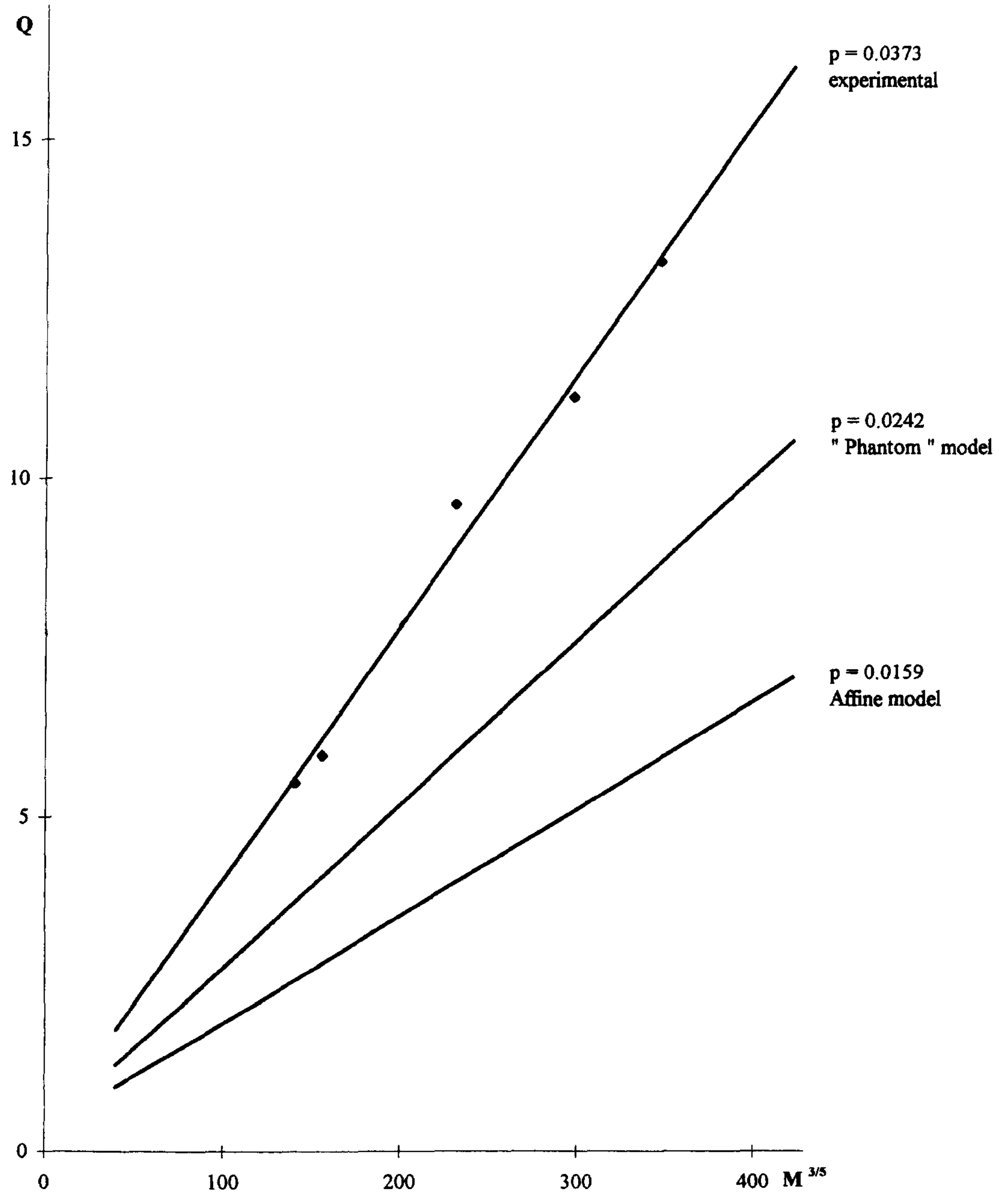


Figure 5 Variation of equilibrium volume swelling degree Q in heptane as a function of $M^{3/5}$ for poly(dimethylsiloxane) model networks. Experimental: slope = 0.0373; affine model: slope = 0.0159; 'phantom' model: slope = 0.0242. The accuracy of the determination of the equilibrium volume swelling concentration is about 3%, whereas the accuracy of the determination of the average molar mass M of elastic chains by light scattering is about 5%

Table 6 Equilibrium volume swelling degree of polystyrene model networks in various swelling solvents. All the networks have been synthesized under standard conditions ($v_c = 0.09$; 3 DVB/LE)

	Q^d		
Swelling solvents	GEL 1947 $M_{LS} = 14\,500^c$	GEL 1977[b] $M_{LS} = 14\,700^c$	GEL 1872 $M_{LS} = 31\,500^c$
Chloroform	13.60	12.70	24.52
Benzene	12.93	12.07	24.34
Tetrahydrofuran	12.50	11.11	22.06
1,2-Dichloroethane	10.45	9.71	18.37
Tetrahydrofurfuryl alcohol	7.04	–	12.56
Cyclohexane	3.15	3.10	3.56

[a] Equilibrium volume swelling degree
[b] Model network prepared with pure *meta*-DVB
[c] Average molar mass of elastic chains determined by light scattering

Table 7 Determination of the interaction parameter for the benzene–polystyrene model network from equilibrium swelling experiments, using the phantom model. Influence of the nature of the swelling solvent

			M = 14 500[a]			M = 31 500[a]			
			χ^c			χ^c		$\chi_0{}^d$	
Sample solvents	$\bar{V}^e$	GEL 1947 Q^{-1b}	$f = 3$	$f = 4$	GEL 1972 Q^{-1b}	$f = 3$	$f = 4$	$f = 3$	$f = 4$
Chloroform	79.18	0.0735	0.4959	0.4809	0.0407	0.4771	0.4586	0.4537	0.4309
Benzene	89.14	0.0773	0.4965	0.4811	0.0410	0.4734	0.4530	0.4473	0.4212
THF[f]	78.82	0.0800	0.5026	0.4903	0.0453	0.4852	0.4698	0.4622	0.4430
1,2-Dichloroethane	81.08	0.0956	0.5147	0.5048	0.0532	0.4945	0.4825	0.4693	0.4545
THFA[g]	96.04	0.1420	0.5409	0.5348	0.0796	0.5136	0.5062	0.4787	0.4697
Cyclohexane	102.92	0.3174	0.6364	0.6352	0.2808	0.6172	0.6163	(0.4699)[h]	0.4712

[a] Average molar mass of elastic chains determined by light scattering
[b] Equilibrium volume swelling concentration $\nu = Q^{-1}$
[c] Interaction parameter for the swelling solvent–polystyrene model network for functionalities f equal to 3 and 4, respectively
[d] Extrapolated value at infinite dilution
[e] Molar volume of the swelling solvent
[f] THF = Tetrahydrofuran
[g] THFA = Tetrahydrofurfuryl alcohol
[h] Underestimated value

concentration considered, if benzene is the swelling solvent. It could be assumed that such a linear dependence, expressed as $\chi = \chi_0 + aQ^{-1}$, should be found for the other swelling solvents. It must be pointed out, though, that this calculation has been carried out with only two networks (samples 1947 and 1972), which obviously implies a lack of accuracy on the slope of the straight lines and on the χ_0 values. Therefore, the extrapolated values of χ_0 should merely be considered as indicative. The data obtained are displayed in *Table 7*. The parameters χ and χ_0 have been calculated for functionalities f of poly(DVB) nodulus equal to 3 and 4, respectively. Equation (24), which corresponds to the phantom model, has been used in this calculation, since, as shown previously, the affine model (equation (23)) is not able to account for the experimental swelling data on polystyrene model networks. For a given functionality, the χ values decrease with increasing values of M for all the swelling solvents. The extrapolated values of χ_0, exhibit a noticeable increase from chloroform to cyclohexane, i.e. from 0.453 (chloroform) to 0.470 (cyclohexane) for $f = 3$ and from 0.431 (chloroform) to 0.471 (cyclohexane) for $f = 4$. These values are quite compatible with the experimental values of the equilibrium volume swelling degree Q and with the thermodynamic quality of the various swelling solvents considered.

CONCLUSION

Syntheses of polystyrene and poly(dimethylsiloxane) (PDMS) model networks have been carried out by endlinking processes. These samples have been synthesized under identical experimental conditions: same concentration upon crosslinking, the functionality of the crosslinks being supposedly identical. The gels merely differ in the average molar mass M of their linear chain elements. They have been swollen to equilibrium in good, intermediate and poor swelling solvents of their elastic chains. In each case, the equilibrium volume swelling degree Q has been carefully determined.

Two different treatments have been put forward to compare the experimental swelling data with those arising from the classical theories of equilibrium swelling, allowing one to draw several conclusions.

(1) For networks swollen to equilibrium in good solvents, such as benzene for polystyrene model

networks and heptane for poly(dimethylsiloxane) model networks, it was found experimentally that Q is proportional to $M^{3/5}$. Using some approximations, it was first established that Q should be a linear function of M^{α}, this linear dependence being strictly expressed as $Q = pM^{\alpha}$. The values of the exponent α can be predicted by both the affine model of Flory–Rehner and the 'phantom' model of James–Guth–Graessley. These two theories include two constants A and B. For the affine model, $A = 1$ and $B = 2/f$, and for the phantom model, $A = (f-2)/f$ and $B = 0$, which leads to different formulations for the two models. For the two binary systems detailed above, it has been found theoretically that the experimental exponent α is equal to 3/5 for both theories.

For benzene–polystyrene model networks, the slope p of the straight line obtained from experimental swelling data is much larger than that arising from the affine Flory–Rehner model, indicating that this model cannot be used to account for the swelling experiments. The case for the phantom model is more favourable. It is observed that the experimental slope and that originating from the phantom model are practically identical, provided the functionality of the crosslinks is located between 3 and 4. This result strongly supports the use of the 'phantom' approach to interpret quantitatively the experimental data on polystyrene model networks swollen to equilibrium in benzene.

For the system heptane–poly(dimethylsiloxane) model networks, the situation is quite different. It has been found that neither the affine model nor the phantom model can account for the swelling experiments, the corresponding theoretical slopes being far from the experimental slope. However, if PDMS model networks are swollen to equilibrium in a poor swelling solvent such as toluene, the Q values become smaller for a given molar mass M of the elastic chains. In that case, the exponent α is equal to 3/8 (instead of 3/5 for a good swelling solvent) and the phantom model equation fits the swelling experimental data fairly satisfactorily.

(2) A more elaborate treatment has been used to interpret the equilibrium swelling data on polystyrene model networks. From the general swelling equation as applied to 'ideal' model networks, it is possible, without any approximation, to calculate the interaction parameter χ between the swelling solvent and the network, using the equations derived from both the affine and the 'phantom' models. In both cases, the variation of χ with respect to the equilibrium volume swelling concentration $v = Q^{-1}$ is linear, in the segment concentration domain considered. This linear dependence can be expressed as $\chi = \chi_0 + aQ^{-1}$, the coefficient χ_0 being the extrapolated value at infinite dilution, which corresponds to the interaction parameter between solvent and linear polystyrene. This calculation has been carried out for various functionalities f of the crosslinks.

For the system benzene–polystyrene model network, it has been demonstrated without ambiguity that the affine model has to be rejected, since the χ_0 values obtained, regardless of the functionality of the crosslinks, are far from the value of χ_0 determined independently for benzene–linear polystyrene. A least-square calculation has been carried out using the χ values derived from the phantom model. In that case, it has been clearly established that the extrapolated values of χ fit well with the expected values of χ_0, for an average functionality f of the crosslinks located between 3 and 4. These results are strong arguments in favour of the phantom model to account for the experimental data.

Ultimately, a similar treatment has been applied to swelling solvents other than benzene. It includes good solvents such as chloroform or THF, intermediate solvents such as 1,2-dichloroethane and poor solvents such as tetrahydrofurfuryl alcohol or cyclohexane. The extrapolated values of χ_0 obtained increase noticeably with decreasing values of the equilibrium volume swelling degree Q of the networks. This increase is quite compatible with the thermodynamic quality of the swelling solvents.

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