Characterization of radical polystyrene gels

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This study deals with the characterization of the structural parameters of radical polystyrene gels by comparing their physicochemical behaviour with ideal polymeric networks prepared by anionic means. To this end, we have assumed that two gels which have the same number of active elastic chains must have the same swelling rate. So as to make the comparison of radical and anionic networks coherent, we have described a two phase model in which a fraction of the network chains is formed by active chains, and the other part is made up of areas with high crosslinking density and low porosity.

INTRODUCTION AND THEORETICAL

Up to this time, networks have been prepared by radical polymerization in which the chain order of the different monomers results from statistical probability, the parameters being concentrations (initiator and monomer) and ratios of radical reactivity. The result is a large distribution of linear sequences between crosslinks and an unknown and varied functionality of the crosslinkage points. Such a method of preparation leads to networks whose structure is not well defined and which, according to certain authors[1,2], can present an inhomogeneous structure.

The physicochemical characterization of a Gaussian network takes place from the following four structural parameters: υ_e, the number of active elastic chains; χ, the Flory–Huggins interaction parameter, solvent–crosslinked polymer, when the sample is at swelling equilibrium in a solvent; f, the functionality of the crosslinks and 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 for the polymer at the crosslinking stage.

The number of experimental tests is, of course, insufficient to characterize all these parameters; this makes it necessary to use simplifying hypotheses which render the description somewhat approximate. In particular, the number of elastic chains is not known precisely, as it depends on the hypotheses adopted and on the experimental conditions. On the other hand, given the complex topology of such networks, the characterization of structural parameters must be carried out in the swollen state so as to minimize intermolecular interactions. This procedure limits the marked influence of entanglements and pendant chains which, in the condensed phase, can be very similar to entanglement.

To ensure a better control of these networks we have made use of an anionic polymerization method developed by Rempp and coworkers[3–5], which makes it possible to synthesize networks whose structures are more clearly defined[6,7]. In particular: (1) polystyrene chains are linear and monodisperse ($\bar{M}_w/\bar{M}_n \approx 1.1$); the molecular weights of these chains can be made to vary in large proportion and can be measured experimentally before crosslinking; (2) the concentration of segments in the gel is equal to the concentration which already existed in the solution before the divinylbenzene was added. Here, the gel point corresponds to multiple linkages between the polymeric chain ends; (3) the total concentration of polymer in its solvent during the crosslinking process can undergo large variations which make it possible to avoid network defects such as pendant chains and entanglements.

Knowledge of this measure seems to facilitate considerably the characterization of the 4 structural parameters. This is made possible because of 3 experimental tests: measurements of the elastic modulus, swelling rate, and by change of the swelling solvent activity[7]. This particular structure of ideal polystyrene networks also makes it easier to understand physical behaviour at a molecular level[6,7]. It therefore seemed interesting for us to make a comparative study of anionic and radical networks.

It has been shown[6] that when a swollen sample is submitted to unidirectional stress (force per unit swollen and strained cross-section) near the instantaneous stress, σ_0, obtained after deformation Λ_x [either elongation ($\Lambda_x > 1$) or compression ($\Lambda_x < 1$)], we can define:

$$\sigma_0 = A q_0^{-2/3} q_i^{-1/3} \upsilon_e^* RT |\Lambda_x^2 - \Lambda_x^{-1}| \tag{1}$$

in which $\sigma_0 |\Lambda_x^2 - \Lambda_x^{-1}|^{-1} = A q_0^{-2/3} q_i^{-1/3} \upsilon_e^* RT$ represents the experimental modulus, G_{ex}.

According to Flory, Wall, and Hermans, $A = 1$:

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

where q_c^{-1} is the volume fraction of polymer at the crosslinking stage; q_i is the swelling ratio of the network and $\langle r_{OS}^2 \rangle$, $\langle r_D^2 \rangle$, $\langle r_C^2 \rangle$ are the mean square end-to-end distances of network in the swollen reference state, dry isotropic state and after crosslinking, respectively.

υ_e^* is the concentration of network chains (per unit dry volume) and $\Lambda_x = L/L_i$ where L_i = the initial length of the sample swollen at equilibrium and L = the stressed length of the swollen sample.

EXPERIMENTAL

Preparation of samples

The choice of experimental conditions is linked to the

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Table 1

Gel	STY/ (STY + Bz)	DVB/ STY	Initiator/ Styrene	T(°C)	Time of co-polymerization (h)
945	0.3	0.06	0.01	70	15
1645	0.3	0.05	0.01	70	15
2345	0.3	0.04	0.01	70	15
265	0.3	0.0425	0.007	80	15
2855	0.3	0.05	0.007	80	15
465	0.3	0.03	0.007	80	15
1555	0.3	0.05	0.007	80	15
3055	0.3	0.035	0.007	80	15
665	0.3	0.02	0.007	80	40
2511	0.3	0.04	0.007	80	15
112	0.3	0.03	0.007	80	20
312	0.3	0.055	0.007	80	15
812	0.5	0.035	0.007	60	15
1012	0.5	0.03	0.007	60	15
512	0.5	0.025	0.007	60	15

production of gels with good mechanical properties in the swollen state when measurements of modulus are taken, for crosslinks of varying porosity (or swelling rate).

Thus copolymerization was carried out in benzene for no more than 15 h, which corresponded to a conversion rate in weight of around 85%. The initiator was benzoyl peroxide: other parameters are given in *Table 1.*

Copolymerization took place under an inert atmosphere, in a cylindrical reactor, so that eight parallelepipedic samples (135 x 42 x 4 mm) could be obtained simultaneously. The gels were deactivated by a solution containing some radical acceptor (quinone); then, the styrene homopolymer was removed by successive washings in a large excess of benzene. All samples were swollen to equilibrium in benzene and cyclohexane.

CHARACTERIZATION OF RADICAL GELS

It seems that for anionic gels at swelling equilibrium in benzene, the interaction parameter, χ, is independent of their structure, especially from the crosslinking density and the volume fraction of the network in the swelling solvent[7].

This result permits us to state that, for radical gels, the parameter χ has the same value and barely depends on the porosity of the sample. We have thus to characterize three parameters with the following two tests: the measurement of the swelling rate q_i; the experimental modulus G_{ex}.

The attempts made up to this time can be classed in two catagories.

(1) The characterization of the modulus makes it possible to define the product $v_e^* q_0^{-2/3}$ (equation 1). If we suppose that $q_0 = q_c$ it is easy to calculate v_e^* [8,9].

(2) The second method involves calculation of v_e from the swelling relation (equation 2, ref 6), supposing that the value of q_0 and the functionality f ($f = 4$) are known[10,11].

If these two methods are equivalent, two networks with the same number of elastic chains (or modulus) must have the same swelling rate. The perfect characterization of anionic gels gives some support to either of these methods. The object of this present chapter will be to compare the results obtained for both types of networks, and so find the characterizing method more suited to the structure of radical gels.

Determination of q_0 *for radical gels*

q_0 is linked to the isotropic deformation factor $\langle\alpha^2\rangle_0$ by the relation:

$$q_0^{-2/3} = \frac{\langle r_c^2 \rangle}{\langle r_{OS}^2 \rangle} q_c^{-2/3} = \langle\alpha^2\rangle_0 \tag{2}$$

Consequently, $\langle\alpha\rangle_0$ depends on the volume fraction of polymer at the crosslinking stage. It is then the conversion rate fraction of the reaction $\alpha_T = \alpha(1 - S)$, in which S is the soluble fraction of extractable polymer and α the total conversion rate in terms of weight.

We can define:

$$q_c^{-1} = \frac{m_{ST}\alpha_T}{dz} \left| \frac{m_{ST}\alpha_T}{dz} + \frac{m_{ST}(1 - \alpha_T)}{d_m} + \frac{m_{Bz}}{d_{Bz}} \right|$$

in which m_{ST} and m_{Bz} are the weights of the monomer (styrene) and of the solvent (benzene), respectively. dz, d_m and d_{Bz} are, at the temperature of copolymerization, the densities of the network, the monomer and benzene, respectively, d_m taking into account the soluble fraction of the polymer.

We have neglected to take into consideration the concentration in divinylbenzene which is relatively low compared to the quantities of benzene and styrene.

Thus, we can fix an approximate experimental value for q_0, when $q_0 = q_c$, that is $\langle r_C^2 \rangle / \langle r_{0S}^2 \rangle = 1$. Many researchers use this approximation to calculate the crosslinking density of three-dimensional networks.

Measurements of the elasticity modulus in the swollen state

Elongation was measured by a cathetometer with a precision of ±1/20 mm in a rectangular glass cell filled with solvent, the samples being held by means of metallic clamps. To measure the stress, a calibrated inductive transducer (Model Q 11/100 gP Hottinger Balwin) was used. The signal of the transducer was amplified by means of a carrier wave amplifier (Model KSW/35–5 Hottinger Baldwin) which gives the force after calibration. Thickness was measured by a microscope with a precision of ±5/1000 mm, and other measurements were taken by means of slide callipers with a precision of 1/20 mm. Taking into account all the experimental errors, the elasticity modulus in extension can be calculated to be ±2.5%.

In *Table 2* we have grouped the elasticity moduli obtained in two swelling solvents, benzene and cyclohexane. We have also stated the average molecular weights between crosslinks, $\bar{M}_c = \rho / v_e^*$, using the approximation $q_c = q_0$.

We note that for two swelling solvents, whose thermodynamic behaviour with polystyrene is very different, the values of $\bar{M}_c$ deduced from the elasticity moduli are quite close, in accordance with the theory and results obtained elsewhere for ideal networks[6].

Comparative study of radical and anionic networks

It is well known that in the case of solvents which have close thermodynamic affinity with the polymer, the swelling ratio is notably independent of temperature, and intermolecular contacts between neighbouring chains are negligible. In addition to this, the Flory–Huggins interaction parameter has hardly any dependence on structural parameters (functionality, crosslink density). The high porosity of the chain links conceals to a great extent all structural defects, such

Table 2

Gels	Q_v		G(10^{-3} dynes/cm^3)		$\upsilon_e^* \times 10^5$		$\bar{M}_c$	
	Benzene	Cyclohexane	Benzene	Cyclohexane	Benzene	Cyclohexane	Benzene	Cyclohexane
945	6.26	2.14	764	857	17.31	13.76	6080	7750
1645	8	2.27	603	684	15.59	11.78	6750	8930
2345	9.78	2.46	338	490	9.35	8.67	11 260	12 130
265	10.77	2.97	291	416.6	8.47	8.01	12 425	13 130
2855	11.64	2.98	185	246.5	6.35	5.45	16 550	19 280
465	14	3.34	153.5	211.5	5.09	4.49	20 680	23 450
1555	18.45	3.92	84.8	142.3	3.37	3.38	31 200	31 100
3055	21.54	3.85	52.8	104.3	2.25	2.29	46 650	45 950
665	26	5.38	26.9	50	1.16	1.34	90 250	78 650
2511	12.3	3.38	259	330	7.6	6.09	13 850	17 260
112	22	4.32	38.1	75.2	1.39	1.60	75 680	65 750
312	8.5	3.09	554	689	12.96	11.1	8120	9480
812	12.7	3.29	278	449	5.73	5.72	18 350	18 400
1012	19.4	3.91	118	182	3.03	2.70	34 700	38 900
512	29.7	4.94	29.1	86.5	0.82	1.29	128 750	81 400

as entanglements and pendant chains, which become evident in the condensed phase[7].

Also, the swelling rate of a gel reflects closely the number of elastic chains in the network, just as the measurement of the elasticity modulus does. It is therefore reasonable to consider that two samples having the same swelling rate must have the same modulus, and this independent of experimental conditions.

To make comparison possible between anionic networks (prepared at a concentration of 7.5%) and radical gels (30 and 50%) we have plotted in *Figure 1* the ratio $GQ_{va}^{1/3}/q_c^{-2/3}$ against the apparent experimental swelling rate Q_{va} of the sample.

Two conclusions can be drawn on examination on this Figure. Firstly, at a given swelling rate, all radical gels have a modulus $GQ_{va}^{1/3}/q_c^{-2/3}$, inferior to that of anionic gels. For high moduli, both kinds of gels behave in a similar way, the influence of polydispersity being of less importance. When the porosity of the gels is considerable (low elastic modulus) the difference is notably accentuated. It is even more apparent when pendant chains in anionic networks are taken into consideration, the number of which increases greatly with molecular weight $\bar{M}_n$ between crosslinks[6] (— — — —, *Figure 1*). Thus, two gels with the same swelling rate apparently do not have the same modulus. This anomaly leads up to consider the significance of parameters intervening in the definition of swelling and of elasticity modulus, as we shall see below.

Secondly, we can distinguish no notable influence of concentration, as all the experimental points obtained for gels prepared at concentrations of 30 and 50% are placed on the same curve. This corresponds to a combined effect on the modulus and on the swelling rate.

In *Figure 2*, we have plotted the apparent swelling rate Q_{va} of networks at swelling equilibrium in benzene, against the molecular weight, $\bar{M}_c$, between crosslinks. In this case, we may note a more distinct influence between the two kinds of gels, but the effect of concentration remains imperceptible.

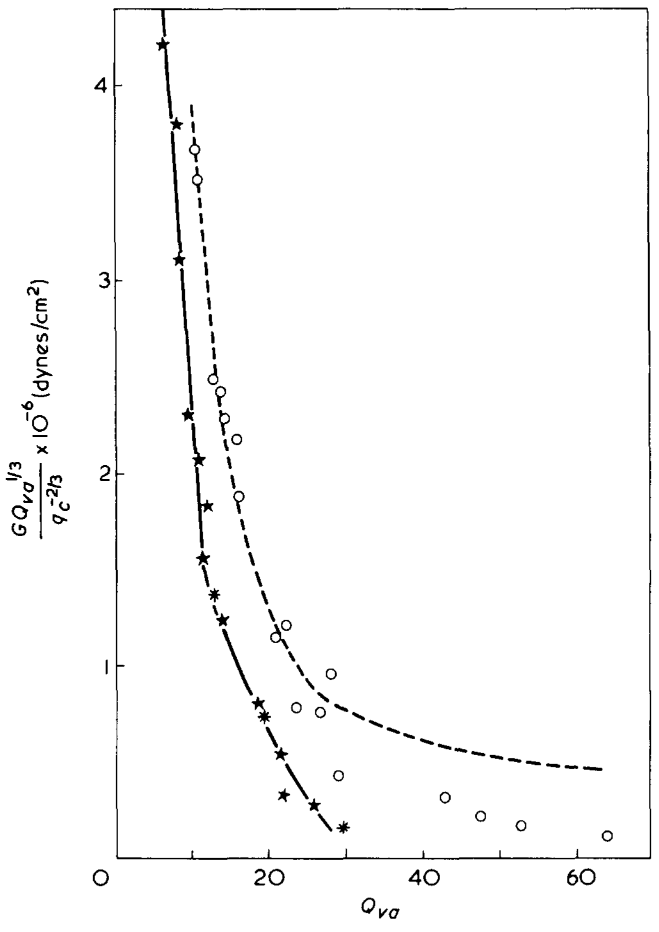

Figure 1 $GQ_{va}^{1/3}q_c^{2/3}$ *versus* the apparent experimental swelling ratio Q_{va} for anionic (○) and radical samples at 30% (★) and 50% (*) concentration at crosslinking stage. — — — —, Ideal

Characterization of radical networks

It is well known that the structure of radical networks is characterized by the high polydispersity of chain links and by a high number of pendant chains. In the formation of a radical polystyrene gel, this high polydispersity is increased because the divinylbenzene monomer polymerizes faster than styrene, their reactivity ratios being different. So, at the beginning of the polymerization, short chain links are built, and the rate [DVB]/[Styrene] becomes smaller and smaller. Accordingly, the crosslinking density is no longer uniform. We have the formation of some areas with high

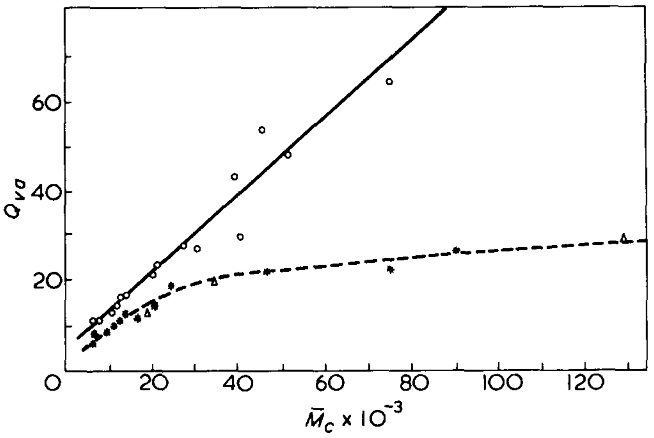

Figure 2 The apparent swelling ratio Q_{va} *versus* $\bar{M}_c$ for anionic and radical gels in swelling equilibrium in benzene. ○, Anionic; *, radical, c = 30%; △, radical, c = 50%

crosslinking density and low porosity. Then we can suppose that the solvent diffuses to a high proportion only in chain links of sufficient porosity. We can roughly describe the behaviour of the network with a two-phase model, one phase formed by all the active elastic chains, whereas the other takes into account the shortest chain links that are inelastic. The latter, which does not contribute appreciably to the swelling ratio of the network, does have an effect on the experimental value of the swelling ratio of elastic chain links to an extent which is in proportion to this value. So the experimental swelling rate is only an apparent swelling rate which does not take into account the real three-dimensional expansion of elastic networks.

A simple calculation allows us to obtain the real swelling ratio Q_{vr} in relation to the apparent swelling Q_{va} and to the volume fraction, Z, of the polymer representing the effective elastic chains of the swollen gel. This parameter thus represents a total volume fraction of the polymer in the swollen network.

Let P be the volume of the polymer corresponding to elastic chains, p the volume of the crosslink polymer which participates neither in the swelling nor in the elastic modulus and H the volume of the solvent absorbed by the polymer.

Thus we have:

$$Z = \frac{p}{P+p} \qquad 0 < Z < 1$$

$$Q_{va} = \frac{P+p+H}{P+p} \text{ and } Q_{vr} = \frac{P+H}{P}$$

From these three equations, we can deduce a relationship between Q_{va}, Q_{vr} and Z:

$$Q_{vr} = \frac{Q_{va} - 1}{Z} + 1 \tag{3}$$

On the other hand v_e^* is a number of elastic chains per unit volume of dry polymer. We have to admit that this volume is that of active elastic chains. This brings us to state that, for radical gels, only a fraction Z of this volume corresponds to the elastic chain links of the network. We thus define a new number of elastic chains, $v_e'^*$, as follows:

$$v_e'^* = v_e^*/Z \text{ or } \bar{M}_c' = Z\bar{M}_c \tag{4}$$

We therefore have a system of two equations with three parameters: Q_{vr}, $v_e'^*$ and Z (equations 3 and 4).

This problem can be solved if we use the following hypothesis. Two gels having the same swelling ratio must contain the same number of elastic chains. We therefore know the curve showing the swelling ratio Q_{vr} against the molecular weight $\bar{M}_n$ between crosslinks for ideal networks (*Figure 2*). It is therefore possible, in the case of radical networks, to determine the values of Q_{vr}, $\bar{M}_c'$ and Z which will characterize them. To this end, we have only to trace, from each of the experimental points of the radical gels, the theoretical curve $Q_{vr}(Z) = f|\bar{M}_c'(Z)|$ determined with the help of equations (3) and (4). The intersection of this curve with that defining ideal networks leads to the parameters Q_{vr}, $\bar{M}_c'$ and Z as *Figure 3* shows. All the results appear in *Table 3*.

Taking into account the correction suggested in this paragraph, we can write:

$$q_c' = \frac{q_c - 1}{Z} + 1$$

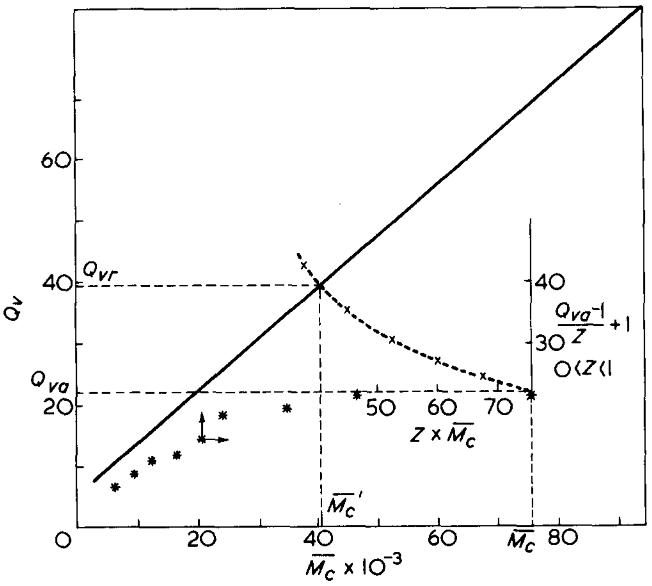

Figure 3 Calculation of the volume fraction Z of effective elastic chains of the swollen radical gel. *, Radical; —, anionic

Table 3

Gel	$\bar{M}_c$	$\bar{M}_c'$	Q_{va}	Q_{vr}	Z
945	6080	4740	6.26	7.74	0.78
1645	6750	5840	8	9.2	0.84
2345	11 260	9000	9.78	12	0.80
265	12 425	9950	10.77	13.2	0.80
2855	16 550	12 400	11.64	15.2	0.75
465	20 680	15 700	14	18.1	0.76
1555	31 200	23 200	18.45	24.3	0.74
3055	46 650	31 300	21.54	31.4	0.67
665	90 250	48 750	26	45.2	0.54
2511	13 850	11 400	12.3	14.5	0.82
112	75 680	40 600	21.8	39.4	0.54
312	8120	6600	8.5	10.2	0.81
812	13 850	13 950	12.7	16.4	0.76
1012	34 700	25 000	19.4	26.5	0.72
512	128 750	64 400	29.7	58.4	0.50

Table 4

Gel	$\bar{M}_c'$	Q_{va}	$q_c^{2/3}$	$q_c'^{2/3}$	$q_0^{-2/3}$	$\frac{\langle r_c^2\rangle}{\langle r_{0S}^2\rangle}$	f (Benzene)	f(Cyclohexane)
945	4740	6.26	2.99	3.29	0.279	0.92	11.73	–
1645	5740	8	3.15	3.36	0.283	0.95	6	–
2345	9000	9.78	3.15	3.42	0.272	0.93	3.21	–
265	9950	10.77	3.21	3.49	0.267	0.93	2.77	4.39
2855	12400	11.64	3.69	4.14	0.222	0.92	4.40	5.78
455	15700	14	3.41	3.76	0.247	0.93	2.36	3.56
1555	23200	18.45	3.62	4.12	0.222	0.92	1.95	2.16
3055	31300	21.54	3.72	4.37	0.203	0.90	2.23	2.41
665	48750	26	3.55	4.56	0.182	0.83	2.54	1.24
2511	11400	12.3	3.05	3.31	0.281	0.93	2.05	3.06
112	40600	21.8	3.14	4.04	0.205	0.83	2.93	2.18
312	6600	8.5	2.74	2.99	0.309	0.92	2.74	3.21
812	13950	12.7	2.12	2.34	0.384	0.90	1.24	2.35
1012	25000	19.4	2.34	2.61	0.343	0.89	0.91	1.91
512	64400	29.7	2.17	2.77	0.284	0.79	0.84	1.34

in which q_c' represents the effective swelling of the network at the time of crosslinking. Therefore:

$$q_0'^{-2/3} = \frac{\langle r_C^2\rangle}{\langle r_{0S}^2\rangle} q_c'^{-2/3}$$

We have calculated the average functionality of the crosslink with the help of swelling rates measured in benzene and cyclohexane. To obtain this result, we have taken the real deformation of elastic chains in the network to be proportional to $Q_{vr}^{1/3}$, the value of which gives a closer idea of the entropic contribution than does the apparent swelling ratio Q_{va}. On the other hand, Q_{va} defines better the state of dilution of the chains if we allow the presence of the non-active chains in the network to contribute to the state of dilution of active chains. The equation of swelling equilibrium can then be written:

$$\log(1 - Q_{va}^{-1}) + Q_{va}^{-1} + \chi Q_{va}^{-2} + \frac{G\bar{V}_1}{RT} - \frac{2}{f}\nu_e^* \bar{V}_1 Q_{vr}^{-1} = 0 \qquad (5)$$

All the results are plotted in *Table 4*. On examination of these results, we can underline the following points.

The calculated functionalities [f(benzene) and f(cyclohexane)] are generally coherent, besides crosslinks 812, 1012, and 512, which probably contain a high proportion of pendant chains. The divergences existing between these two swelling solvents are certainly linked to insufficient influence of the structural parameters in the case of networks of low porosity (cyclohexane), which is the reason for considerable errors in the determination of the functionality. This parameter no longer has a fixed size, linked only to the reactivity of the crosslinks (DVB), but on the contrary, represents a macroscopic magnitude including all of the structural defects (entanglements, pendant chains, etc.). This brings us to a model which describes anionic gels very well and for which the notion of functionality, taken in a wide sense, has no significance, but represents rather a topological parameter in the network[6].

On the other hand, with this two phase model, we can obtain ratios $\langle r_C^2\rangle/\langle r_{0S}^2\rangle$ whose values are all situated between 0.80 and 0.95. The average value, 0.9, is notably higher than that found with anionic gels[6,7] ($\langle r_C^2\rangle/\langle r_{0S}^2\rangle = 0.7$). We know that this relation reflects the influence of crosslinking on the mean square end-to-end distance of network chains in the reference state. It is reasonable to think that with a high concentration of polymeric chains, this influence is not very great, whereas at high dilution, as in the case of anionic gels ($q_c^{-1} = 7.5\%$) crosslinking has a stronger effect. In the

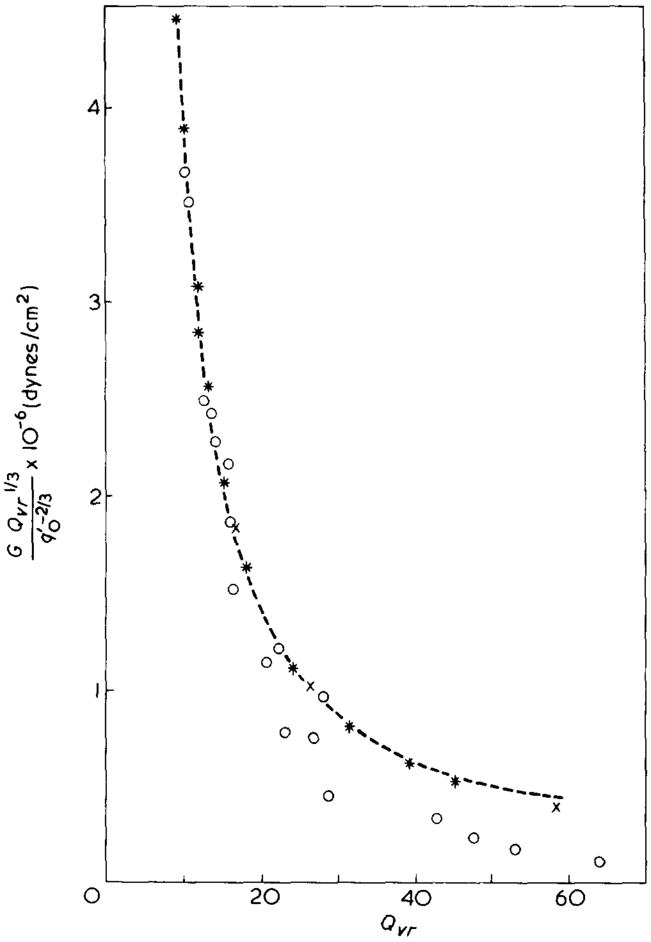

Figure 4 $GQ_{vr}^{1/3} q_0'^{2/3}$ *versus* the real swelling ratio Q_{vr} for anionic (○) and radical samples at 30% (*) and 50% (x) concentration at crosslinking stage. – – –, Ideal

case of ideal networks, the parameters $\langle r_C^2 \rangle$ and $\langle r_{0S}^2 \rangle$ also have a more obvious significance than in that of radical polymerization. As in the definition of the 'memory term', the ratio $\langle r_C^2 \rangle / \langle r_{0S}^2 \rangle$ is independent of the crosslinking density, which corroborates to a great extent, the results obtained with anionic gels[6,7].

So as to check the coherence of the two phase model, we have plotted in *Figure 4* the relation $GQ_{vr}^{1/3}/q_0'^{-2/3}$ against Q_{vr}. This curve shows the perfect similarity in the behaviour of the two types of gels up to a swelling ratio of 20–25. Beyond this value, the anionic gels include an important proportion of pendant chains, and if we take into account these defects in recalculating the modulus of an ideal anionic gel, we note an excellent overlapping of the two curves throughout the experimental area (– – – –, *Figure 4*).

In conclusion, we can say that, despite the rough approximation of this model, the results thus obtained are very satisfying, and corroborate fully those of anionic gels. The number of elastic chains, $\nu_e'^*$, which we calculated in this way reflects more clearly the behaviour of the radical gel than ν_e^*.

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