Specific volume of polystyrene networks

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We have described a method for the measurement of the specific volume of polymer networks at different degrees of swelling. We have observed a very small difference between the apparent specific volume of polystyrene in the swollen gel state and in solution in the same solvent and at the same polymer concentration. This indicates a small variation in the chain expansion with the degree of swelling. Moreover, our precise measurements of the swelling parameters confirm the interdispersion phenomenon as the main process for the swelling in a 'theta' solvent.

Keywords Network; polystyrene; specific volume; swelling; scaling laws; interdispersion

INTRODUCTION

The swelling process of polymeric networks is the subject of numerous controversies. The predictions of the scaling laws of the variation of the swelling parameters with the molecular weight of the network chains differ according to the theoretical approach employed. The classical theories[1-4] predict an affine deformation of the polymer chains which are assumed to be partially collapsed in the network in the dry state compared with the swollen state. More recently, de Gennes[5] has proposed a simpler model based on an analogy between swollen networks and semi-dilute polymer solutions. By starting from this point of view, Bastide *et al.*[6] have shown that the swelling in a θ solvent can be simply explained by the process of chain interdispersion without taking into account changes in the chain conformation.

However, density measurements on polymer solutions[7], have revealed a dependence of the apparent specific volume of the polymer on its conformation. We can explain this phenomenon by assuming that the expansion of the chains due to excluded volume effects induces some changes in the packing of the solvent molecules around the polymer[8]. We would expect that density measurements on model networks would provide useful information concerning the swelling process. The purpose of this paper is to describe the experimental apparatus which allows not only density determination but also very precise measurements of the swelling parameters. We will discuss our preliminary results obtained with trifunctional model networks of polystyrene prepared by one of us[9].

EXPERIMENTAL

Instrumentation

The apparatus is schematized in *Figure 1.* To determine the specific volume of the gel, we simply use the buoyancy method either in the swelling solvent or in a non-solvent. As we need, at each swelling step, the weight and volume of the sample, this method is also appropriate in measuring the volume and weight swelling degrees of the gel as a function of time with a high accuracy.

The principal part of the experimental apparatus is a microbalance Mettler ME21 with magnetic control. The accuracy is ±0.4 μg for a total weight variation equal to 2 mg. Under the balance scale a nickel wire is attached, B, for the gel suspension. This wire must be a good conductor to avoid electrostatic interactions with the glass since it passes through a long glass tube to the solvent reservoir, A. On both sides of the tank, two outlets allow the emptying and filling by teflon tubes, C, connected to a peristaltic pump, D, and to other thermostated solvent tanks, E. The sample, S, is supported by the wire. The detection is made by a recorder I. The upper part of the balance, G, and the measurement cell, A, are separately thermostatically controlled by two circulation thermostats, T, to an accuracy of 10^{-2}°C. Thus the measurements can be performed at high temperature without modifying the balance equilibrium. Both temperatures are controlled with a Hewlett Packard quartz thermometer.

General procedure

A cylindrical sample (diameter = 1 cm, height = 1 cm) is carefully cut from the gel immersed in benzene and pierced along its axis by the nickel wire. If the measurements are carried out in benzene, the sample is immediately placed in the cell in an excess of swelling solvent and held for 24 h at the chosen temperature before performing measurements. If another solvent is used, the gel is first slowly dried in the balance until a constant weight is attained and then immersed at the chosen temperature for the time necessary to reach equilibrium swelling.

Measurements at swelling equilibrium. The solvent is rapidly evacuated and the registered weight variation Δm_1 is equal to the difference of Archimedes' buoyancy exerted by the solvent and air on the sample

$$\Delta m_1 = (V_G + v)(d_1 - d_2) \qquad (1)$$

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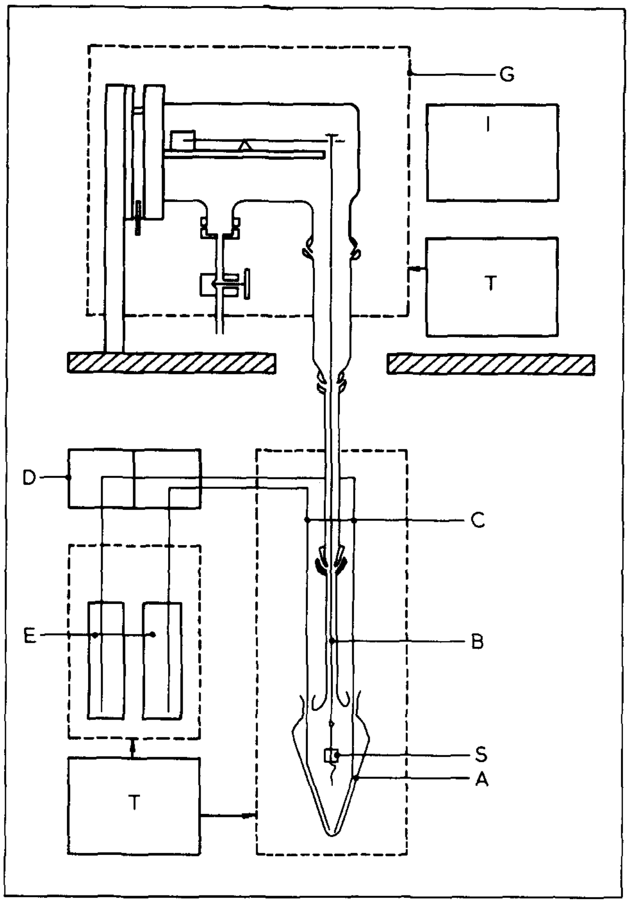

Figure 1 Experimental apparatus. Explanation of the symbols given in the text. (— — — —) Thermostatically controlled jacket

where V_G is the volume of the swollen sample, d_1 the solvent density, d_2 the density of air (in fact, saturated vapour of the given solvent) and v the volume of the immersed wire. v is previously determined by following the same procedure in the absence of the gel sample and by adjusting the solvent height in the reservoir at the same level. The densities d_1 and d_2 are measured on a digital densitometer DMA 02, improved in our laboratory[10]. The same measurement gives m_g, the mass of swollen sample and its specific volume $\bar{v}_g = V_G/m_g$. By assuming that the specific volume of the solvent, $\bar{v}_s$, remains constant during swelling, we can determine, from $\bar{v}_g$, the apparent specific volume φ_2 of the polymer in the gel.

$$\bar{v}_g = (1 - c_w)\bar{v}_s + c_w\varphi_2 \qquad (2)$$

To determine, c_w, the weight concentration of the polymer, we need the swelling parameters of the gel obtained from measurements carried out on the dried samples.

Measurements on dried samples. The sample was slowly dried under vacuum and heated for several hours at 120°C above the glass transition temperature to eliminate completely the strongly adsorbed solvent. We then measured the mass, m_s, of the dried sample and after immersion in a non-solvent, we could determine its volume V_s, from the measurement of the Archimedes' buoyancy. The density of the liquid must be lower than the gel density. For polystyrene gels, we obtained reproducible measurements with methanol.

In order to verify the validity of our technique we measured the specific volume of a dried sample by classical dilatometry. In *Figure 2*, we can see the good agreement obtained by the two experimental procedures. We can calculate swelling parameters as follows:

$$Q = \frac{V_g}{V_s} \quad \text{and} \quad G = \frac{m_g}{m_s} \qquad (3)$$

and the specific volume of the dried sample

$$\bar{v}_a = \frac{V_s}{m_s} \qquad (4)$$

Determination of the apparent specific volume φ_2 of polymers in the swollen gel. Relation (2) can be rewritten

$$\bar{v}_g = \left(1 - \frac{1}{G}\right)\bar{v}_s + \frac{\varphi_2}{G} \qquad (5)$$

$\bar{v}_g$ is also equal to

$$\bar{v}_g = \frac{V_g}{m_s G} \qquad (6)$$

and by using relation (4), we obtain:

$$\varphi_2 = Q\bar{v}_a - \bar{v}_s(G - 1) \qquad (7)$$

Measurements for intermediate swellings. We have carried out some measurements during deswelling of the networks, in air, and after rapid immersion of the dry polymer in the given solvent. At each time, we used the same procedure as for the swelling equilibrium; we determined Q_i, G_i and $\bar{v}_{gi}$ and by using relation (7) and replacing Q and G by Q_i and G_i, we obtained the variation of φ_2 as a function of c_w. In these conditions, the state of swelling of the samples is probably not as uniform as at equilibrium and the measurements correspond only to an average concentration c_w in the samples. Nevertheless, if this effect of gradient concentration in the gel can be

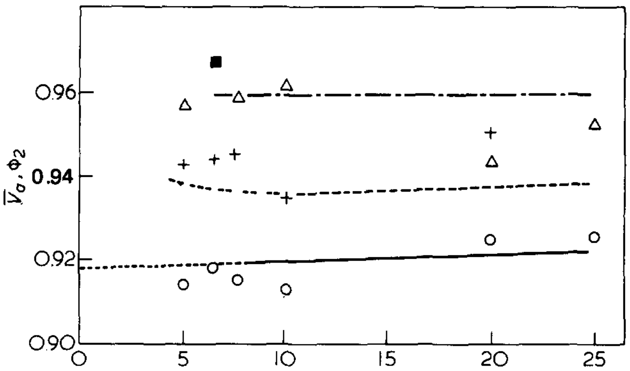

Figure 2 Variation of the specific volume, $\bar{V}_a$, of the dry gels and apparent specific volume ϕ_2 of the networks at swelling equilibrium as a function of the reciprocal molecular weight of the chains. Networks swollen in benzene at 25°C (○) and in cyclohexane at 34.5°C (+); dry networks (△) dilatometric measurement (■). Curves for linear polystyrenes in benzene solutions at 25°C (———), in cyclohexane solution at 34.5°C (— — —) and in the glassy state (—·—·)

Table 1 Batch characteristics and experimental results

Batch	GPST 8	GPST 3	GPST 2	GPST 4	GPST 9	GPST 7	Comment
Q	12.40	13.67	14.80	16.32	19.54	19.44	Benzene 25°C
$G = 1/c_W$	10.50	11.45	12.65	13.87	16.70	16.45	
d_s	0.873257	0.873337	0.873375	0.873377	0.873352	0.873367	
C_E (g cm^{-3})	0.0848	0.0776	0.0702	0.0639	0.0529	0.0537	
$\bar{v}_2$	0.926	0.925	0.913	0.915	0.918	0.914	
$\bar{v}_a$	0.952	0.943	0.963	0.959	0.967	0.957	Dry
Q	2.78	3.70	4.19	4.6	5.44	5.77	Cyclohexane 35°C
$G = 1/c_W$	2.31	2.94	3.37	3.678	4.30	4.50	
d_s	0.764482	0.764495	0.764490	0.764504	0.764491	0.764496	
c_E = (g cm^{-3})	0.3777	0.2865	0.2437	0.2245	0.1901	0.1809	
$\bar{v}_2$	0.933	0.951	0.935	0.946	0.944	0.943	
M_s	4.000	5.000	10.000	13.000	15.400	20.000	Osmometry
ϕ^{-1} ($t = 1$)	5.02	4.41	3.55	4.05		6.93	Reference

neglected for a slight deswelling, with all the polymer chains remaining in the rubbery state, it becomes important for high polymer concentrations for which a part of the sample approaches the glassy state. For this last case, it is difficult to interpret the results.

Accuracy of the method

The accuracy of the method is dependent on two factors:

(1) The precision given by the experimental device on one sample; this can be determined by performing the measurements on the same sample several times.

(2) The reproducibility obtained by studying different cylinders cut off from different parts of the prepared network. Under these conditions, the variation obtained on φ_2 did not exceed $\pm 2 \times 10^{-3}$ cm^3 g^{-1}. For measurements performed on polymer solutions by use of a densitometer, the estimated accuracy is $\pm 5 \times 10^{-4}$ cm^3 g^{-1} for the same systems polystyrene–benzene or polystyrene–cyclohexane.

Samples

We have studied a series of trifunctional model gels prepared according to a method described elsewhere[9]. Their characteristics are reported in *Table 1*. The solvents, benzene, cyclohexane and methanol were distilled and their purity was tested by densitometric measurements. All our experimental results are reported in *Table 1*.

RESULTS

Apparent specific volume

In *Figure 2*, we have reported the variation of φ_2 (relation (7)) as a function of $1/M_s$, M_s being the molecular weight of the network chains for a swelling equilibrium in benzene and cyclohexane. On the same plot, we have drawn the curves for linear polystyrenes in solution in the same solvents and for the same polymer concentration obtained in our previous investigations[7]. If we take into account the accuracies of the measurements discussed above, the two types of behaviour seem to be very similar. The slight increase of φ_2 with decreasing M_s, in networks, indicates that the chemical units present at branch points are probably less dense than the polystyrene units. The variation of φ_2 *versus* polymer concentration c_w is shown in *Figure 3*, for two network samples; this can also be compared with the variation obtained for linear polystyrene chains of the same molecular weight with that for the network chains. Again, we observed no significant differences between networks and solutions.

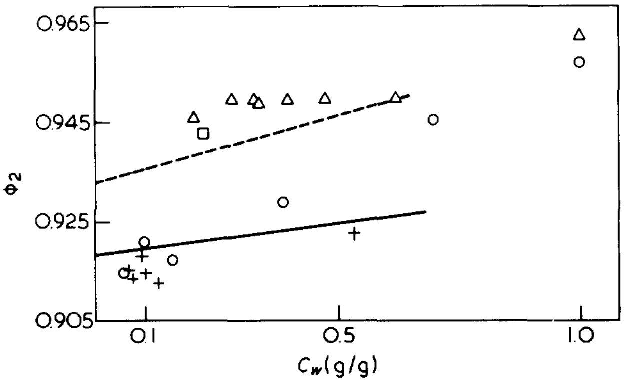

Figure 3 Concentration dependence of φ_2; network samples GPST 7 and GPST 4 swollen in benzene (○, +) and in cyclohexane (□, △); linear polystyrenes in benzene (———) and in cyclohexane (– – –)

The values of specific volume $\bar{v}_a$ corresponding to the dry gels are also reported in *Figure 2* and *Table 1*. They are in good agreement with those determined for an uncrosslinked polymer in the glassy state (~0.950–0.960 cm^3/g). A very precise comparison would not be very significant since it is well known that the measurement of the specific volume of a polymer in the glassy state depends on the thermal history of the sample. Nevertheless, the polymer chains, either crosslinked or free, seem to have the same behaviour. One can assume that below the transition temperature, the specific volume has the same value in both cases and the mixing volume excess should also be identical.

All our previous results concerning the volume effects in polymer solution leads us to the conclusion that a relation exists between the apparent specific volume and the chain conformation. More precisely, the fundamental parameter is the expansion, α, of the chains. For instance, in a dilute regime, a high molecular weight polymer ($\alpha = 2$) has $\varphi_2 = 0.900$, whereas $\varphi_2 = 0.918$ for samples with a molecular weight lower than 2×10^4. In the same way, the variation of φ_2 with polymer concentration, c_w, is dependent on the molecular weight. When α is expected to decrease strongly with c_w, we observe also an important variation in φ_2. This is the case for high molecular weight polymers. If α remains constant over the whole concentration range (for $M < 2 \times 10^4$), the variation of φ_2 is much less important.

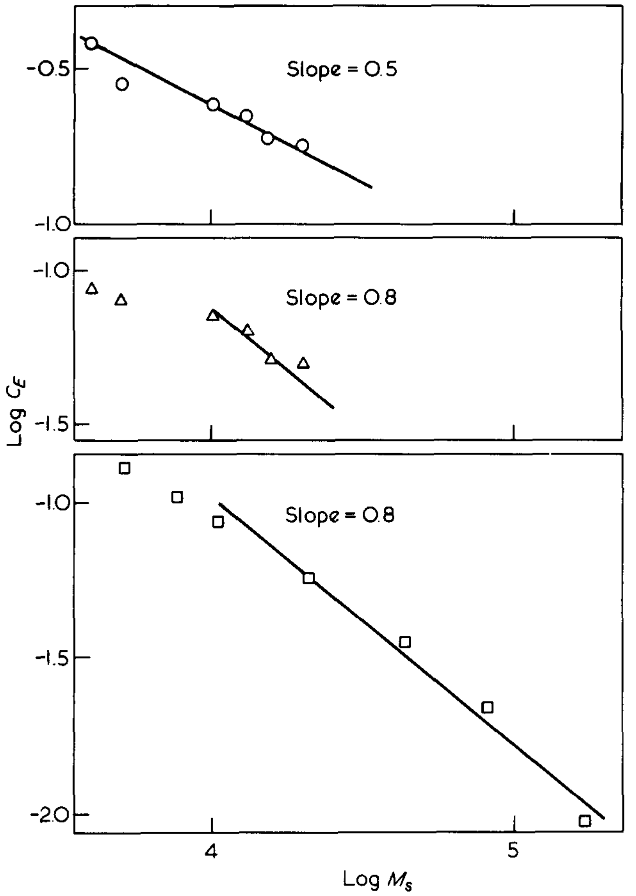

Figure 4 Logarithmic plots of the equilibrium concentration $c_E = f(M_s)$ for networks swollen in cyclohexane (○) and in benzene (△) (this work), networks of ref. 12 swollen in benzene (□)

In early theories on network swelling, it has been assumed that the chains are unperturbed in the reference state and 'supercoiled' in the dry state. Neutron scattering experiments[11] performed on polystyrene networks containing a proportion of labelled chains, have not revealed such conformational changes. In fact, in the dry state, the dimensions of the chains have been found to be unperturbed. Moreover, studies of networks with labelled branch points have shown a $M_s^{1/2}$ dependence of the average distance between nearest neighbouring crosslinks, *h*, corresponding to a Gaussian statistic of the chains even in a good solvent. This is in agreement with the fact that, in the range of molecular weight generally investigated ($M_s < 20\,000$) the excluded volume affects must be very small. Bastide *et al.*[6] proposed for the network swelling a chain interdispersion process instead of an affine deformation.

Our measurements of φ_2, on crosslinked systems compared with those on solutions seem to confirm such a hypothesis (see *Figure 3*). Indeed, φ_2 values are of the same order of magnitude and since φ_2 is known to be very dependent on α for polymer in solutions, this result suggests a slight expansion of the chains at equilibrium swelling and a small variation with the degree of swelling. Let us say that the φ_2 values of networks swollen in benzene are slightly lower than those observed in benzene solutions for the higher M_s values. If the accuracy of our measurements were better, we might conclude that some extension of the chains occurs due to the network effect, but such a conclusion should be considered with caution at this stage.

Volume fraction of polymer at equilibrium swelling

In the classical approach, which takes into account a memory parameter φ_C, the volume fraction of polymer φ_0 at equilibrium swelling is predicted to vary as

$$\varphi_C \propto \varphi_0^{2/5} M_s^{-3/5} \tag{8}$$

The treatment of de Gennes based on an analogy with semi-dilute solutions identifies the equilibrium concentration c_E (g cm^{-3}) with the concentration c^* of a solution of polymer of the same molecular weight as the chains of the network

$$c^* \propto c_E \propto \frac{M_s}{R_G^3} \tag{9}$$

where R_G is the radius of gyration of such macromolecules in the dilute region in a good solvent. One can expect

$$c_E \propto M_s^{-1/2} \quad \text{in cyclohexane} \tag{10}$$

and $C_E \propto M_s^{-4/5}$ in a good solvent, if one considers $R_G \propto M^{3/5}$. In *Figure 4* the logarithmic plots of $C_E = f(M_s)$ obtained from our measurements of Q and G are represented. For cyclohexane the experimental results are in good agreement with the de Gennes predictions whereas, for benzene, the slope is much higher than $-\frac{4}{5}$. For comparison we have calculated from previous studies of Weiss *et al.*[12] the M_s dependence of C_E for polystyrene networks obtained with divinylbenzene as a crosslinking agent. In this case also, the experimental slope differs from $-\frac{4}{5}$ but for higher molecular weight it tends towards this limit. In fact, in the range of molecular weights studied in the present work ($M_s < 20\,000$), the excluded volume exponent ν ($R_G \propto M_s^{\nu}$) is probably lower than its asymptotic limit for high values of M_s.

Bastide *et al.*[6] have calculated the limiting volume fraction of polymer in a swollen gel according to the process of chain interdispersion without any change in the chain conformation

$$\varphi' = \frac{F}{4} \frac{V_s}{a^3} M_s^{-1/2} = \frac{1}{Q} \tag{11}$$

where F is the functionality of the network, V_s the volume of the statistical segment of length a. *Figure 5* shows excellent agreement between the experimental points and the calculated curves, for networks swollen in cyclohexane. The difference between the degrees of swelling in benzene and cyclohexane may be due to some expansion of the chains related to excluded volume and

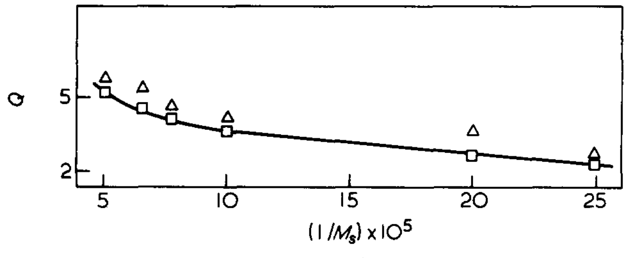

Figure 5 Experimental values of Q (△) for networks swollen in cyclohexane. Curve $Q = f(1/M_s)$ calculated from relation (11) (–□–)

network effects. The low values of φ_2 observed for samples in benzene at swelling equilibrium could be explained by such a phenomenon.

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