Scaling laws and polystyrene networks: a quasi-elastic light scattering study

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Randomly crosslinked networks with a range of crosslink densities were prepared by γ-irradiation. Quasi-elastic light scattering measurements were made on the gels swollen to equilibrium in cyclohexane at 308, 318 and 333 K. The longitudinal osmotic modulus M_{os} was obtained from the intensity of the dynamically scattered light, and the cooperative diffusion coefficient D_c calculated from the relaxation rate of the autocorrelation function. The concentration dependence of these parameters at the theta temperature was found to be consistent with the scaling predictions, but at higher temperatures where excluded volume conditions prevail, deviations from scaling behaviour were observed. These discrepancies are probably caused by defects in the network structure.

(Keywords: scaling; networks; light scattering; polystyrene)

INTRODUCTION

The response of swollen networks, gels and semidilute polymer solutions to perturbations has often been taken to be equivalent as long as the lifetime of the physical entanglements of the macromolecules is greater than the reciprocal frequency of the perturbation[1-3]. This analogy is inherent in the de Gennes 'c^* theorem'[4], whereby above a critical overlap concentration, c^*, the properties of solutions and gels are described by universal scaling laws, the important length scale of which is the correlation length ξ. Much examination of the application of scaling laws and mean field theories to polymer solutions has been undertaken using small angle neutron scattering[5-7]. Rayleigh light scattering from polymer gels and semi-dilute solutions has also been used to investigate the applicability of scaling laws, particularly quasi-elastic light scattering (QELS). While it is well known that QELS provides a diffusion coefficient, Geissler and Hecht[8-10] have shown that by suitable calibration, the absolute intensity at zero time delay can be obtained from the same measurements. The collective diffusion coefficient D_c and the longitudinal elastic modulus M_{os} obtainable from such experiments are directly related to the correlation length ξ. By examining the concentration dependence of these two parameters, the applicability of the scaling laws may be tested.

We report here the results of a series of QELS measurements on randomly crosslinked polystyrene networks at varying degrees of equilibrium swelling. These data are part of a wider investigation of the application of classical elasticity theory and of scaling laws to polymer gels[11].

LIGHT SCATTERING FROM POLYMER GELS

The detailed theory of Rayleigh light scattering from gels has been given by Tanaka *et al.*[12] and more recently by Nossal[3]. The field autocorrelation function for polarised light scattered by density fluctuations in the sample is given by

$$I(t) \propto \frac{1}{M} \exp(-\Gamma t) \tag{1}$$

where M is the longitudinal elastic modulus of the gel and Γ is the relaxation rate of the autocorrelation function. In a swollen polymer network, or a concentrated polymer solution, the elastic modulus relevant to concentration fluctuations, M_{os}, has two components[13,14]

$$M_{os} = K_{os} + \frac{4}{3} G \tag{2}$$

where K_{os} is the bulk osmotic compressibility of the swollen network and G is the shear modulus. The relaxation rate of the autocorrelation function is related to the cooperative diffusion coefficient D_c and the polymer volume fraction of the gel ϕ_p by

$$\Gamma = D_c Q^2 (1 - \phi_p) \tag{3}$$

where Q is the scattering wave vector of the light. The factor $(1 - \phi_p)$ corrects for the displacement volume of the polymer[15], and equation (3) assumes that heterodyne conditions prevail (see Experimental section).

In certain inhomogeneous systems, the autocorrelation function cannot be described by a single exponential of the form of equation (1). It is then useful to perform a

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cumulant analysis of the spectra[16], whereby the autocorrelation function is expressed in the form

$$\log I(t) = A - \bar{\Gamma} t + \mu_2 t^2/2! + \ldots \qquad (4)$$

In this case, the first cumulant, $\bar{\Gamma}$ is used in equation (3) to define D_c. The determination of M_{os} is obtained from the constant A of equation (4), after calibration of the spectrometer with a concentrated polymer solution for which the osmotic modulus is known[8,9].

Scaling laws for M_{os} *and* D_c

The dependence of the osmotic modulus and diffusion coefficient on polymer volume fraction is described by scaling laws proposed by de Gennes[4,17]. The polymer solution (or gel) is viewed as an assembly of close packed correlation spheres of radius ξ. For gels fully swollen in a solvent, both K_{os} and G are proportional to $k_B T/\xi^3$, where k_B is the Boltzmann constant. The cooperative diffusion coefficient, on the other hand, is given by

$$D_c = k_B T / 6\pi\eta_s\xi \qquad (5)$$

where η_s is the viscosity of the pure solvent and T the absolute temperature.

The scaling laws describing $\xi(\phi_p)$ depend on the strength of the excluded volume effects. In thermodynamically good solvents (large excluded volume)

$$\xi \propto \phi_p^{-0.75} \qquad (6)$$

and hence

$$M_{os} \propto \phi_p^{2.25} \qquad (7)$$

and

$$D_c \propto \phi_p^{0.75}$$

In theta solvents, the excluded volume is zero, and the corresponding relations are

$$\xi \propto \phi_p^{-1}$$
$$M_{os} \propto \phi_p^{3} \qquad (8)$$
$$D_c \propto \phi_p$$

Although these scaling laws have been confirmed by small angle neutron scattering from particular polymer–solvent systems, discrepancies have been observed[7]. Some of these data have been rationalized with the earlier mean field theory of Edwards[18], whilst Schaeffer[19] has considered them as evidence for a 'marginal' regime of excluded volume in which $\xi \propto \phi_p^{-0.5}$.

EXPERIMENTAL

Network preparation

Linear atactic polystyrene with $M_w/M_n < 1.1$ was prepared by anionic polymerization in tetrahydrofuran solution. The weight average molecular weight, M_w, determined by gel permeation chromatography, was $\approx 10^5$ Daltons. Discs approximately 1 mm thick were prepared by compression moulding the polymer into an evacuable mould, followed by heating to 450 K and then cooling below the glass transition temperature whilst in the press. A number of discs were placed in ampoules which were then evacuated and flame sealed. The ampoules were subsequently γ-irradiated in a ^{60}Co source at ambient temperature at a dose rate of 5×10^3 Gy h^{-1}. Total doses were between 2 MGy and 10 MGy. The gel point dose for the molecular weight of polystyrene used was 2 MGy. After irradiation the polystyrene discs were exhaustively extracted with cyclohexane and toluene to remove sol fraction and then carefully dried.

Quasi-elastic light scattering

The QELS apparatus, described in detail elsewhere[8,9], had as light source a 15 mW Spectra Physics SP124B He–Ne laser. The light scattered at 90° to the incident beam was collected in one coherence area by a photomultiplier, and the signal sent to a 128 channel correlator working in the zero clipping mode. The incident light intensity was monitored using a beam splitter and a photovoltaic cell.

The specimens were contained in rectangular quartz cells with a 2 mm path length, housed in a copper jacket whose temperature was controlled by a Peltier effect device. Gel samples, previously swollen in cyclohexane at the desired temperature between 308 and 333 K were then placed in the cell with excess solvent and the cell sealed and kept at the chosen temperature for 24 h. To ensure heterodyne detection, scattering volumes in the sample were chosen to include bright spots arising from adventitious dust particles trapped in the gels. To enable calculation of the osmotic modulus, calibration of the spectrometer was made using a solution of polystyrene in cyclohexane for which the osmotic modulus was known[20].

The scattered signal from the gels was such that experimental durations of the order of 20 min were necessary, with clock periods between 2 μs and 8 μs. For each combination of network and temperature, between 5 and 12 spectra were recorded, using a different scattering volume each time.

RESULTS

The intensity autocorrelation function of the scattered light was analysed using a two cumulant expansion[16] (c.f. equation (4)), and the intensity at zero delay time obtained from the extrapolation of the curve fitted to the data. *Figure 1* shows a typical spectrum together with the fit of the two cumulant expression to the data. The variation of the correlation function with network conditions was qualitatively consistent with trends reported from other polymer networks[21], namely a decrease in intensity at zero time delay as the swelling ratio of any network was increased by increasing the temperature, whilst for any one temperature the intensity decreased as the total irradiation dose increased (i.e. as crosslink density increased). *Figure 2* shows a plot of the variation of D_c as a function of polystyrene volume fraction. Lease squares analysis of these data gives:

$$\begin{aligned} &308\ \text{K:} \quad D_c(\text{m}^2\text{s}^{-1}) = (2.3 \pm 0.4) \times 10^{-10}\, \phi_p^{(1.17 \pm 0.15)} \\ &318\ \text{K:} \quad D_c(\text{m}^2\text{s}^{-1}) = (1.9 \pm 0.4) \times 10^{-10}\, \phi_p^{(0.67 \pm 0.1)} \\ &333\ \text{K:} \quad D_c(\text{m}^2\text{s}^{-1}) = (2.5 \pm 0.4) \times 10^{-10}\, \phi_p^{(0.46 \pm 0.12)} \end{aligned} \qquad (9)$$

Figure 3 is a log–log plot of the osmotic modulus calculated from the light intensity at zero time delay.

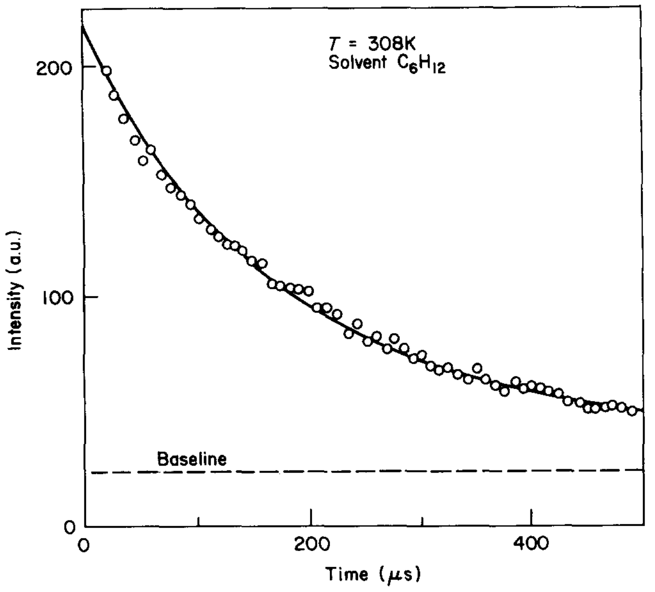

Figure 1 Typical intensity autocorrelation function for light scattered at 90° from a swollen polystyrene network. (———) Computer generated fit of a two cumulants expression to the data

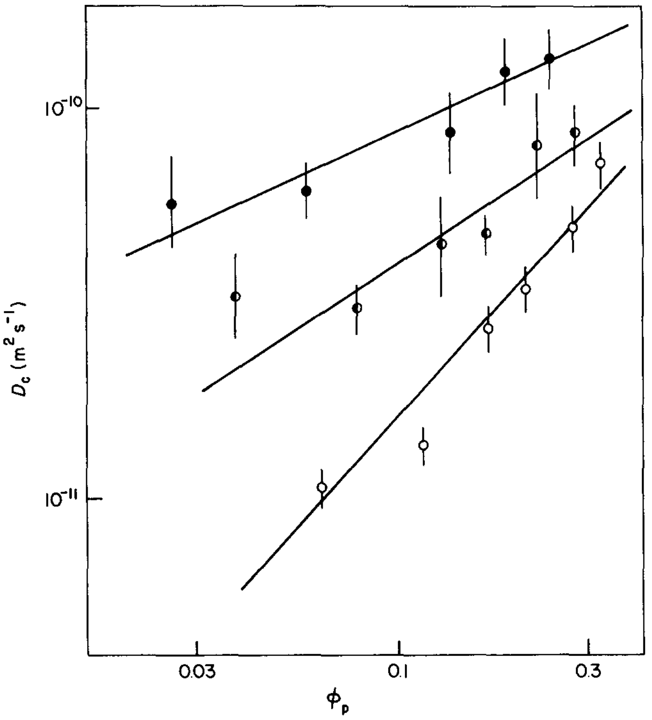

Figure 2 Cooperative diffusion coefficient, D_c, as a function of polymer volume fraction, ϕ_p, for polystyrene networks swollen to equilibrium in cyclohexane. ○ 308 K; ◐ 318 K; ● 333 K

Unlike the diffusion coefficient, the data appear to show little variation with temperature, and the least squares line through *all* the data points is

$$M_{os}(\mathrm{Nm}^{-2}) = (4.7 \pm 0.8) \times 10^6 \phi_p^{(2.6 \pm 0.1)}$$

When the data from each temperature are analysed separately, one obtains

$$\begin{aligned} &308\,\mathrm{K}: \quad M_{os}(\mathrm{Nm}^{-2}) = (6.5 \pm 2.3) \times 10^6 \phi_p^{(2.9 \pm 0.2)} \\ &318\,\mathrm{K}: \quad M_{os}(\mathrm{Nm}^{-2}) = (4.4 \pm 1.1) \times 10^6 \phi_p^{(2.62 \pm 0.15)} \qquad (10) \\ &333\,\mathrm{K}: \quad M_{os}(\mathrm{Nm}^{-1}) = (6.9 \pm 1.8) \times 10^6 \phi_p^{(2.62 \pm 0.11)} \end{aligned}$$

The estimates of M_{os} obtained in this way have generally been found to agree within about 20% of the value obtained by other methods[8,9,22]. It seems probable thereafter that the error corresponds roughly to the scatter in the present data.

DISCUSSION

The osmotic modulus M_{os}

A notable feature of these experiments is that in the concentration range examined, the curves $M_{os}(\phi_p)$ for different temperatures lie very close to each other. This behaviour is not unexpected, since, from equations (7) and (8), a crossover concentration must exist in which the theta behaviour of M_{os} ($\propto c^3$) must intersect the good solvent behaviour ($\propto c^{2.25}$). The data for the theta temperature of this system (308 K) gives an exponent (2.9 ± 0.2) which is consistent with the theoretical value, but full confirmation requires more data at this temperature. The theoretical exponent of 2.25 for good solvent conditions has been observed for polystyrene gels swollen in benzene[23] as well as for polyacrylamide gels swollen in water[9]. Earlier neutron scattering data[7] for the static correlation length of *solutions* of polystyrene in cyclohexane suggested that over the temperature range 318 K to 333 K, marginal behaviour (i.e. weak excluded volume) is obtained. No evidence for this is noted in the present data. The slope of our higher temperature data corresponds to a scaling exponent of $2.6_2 \pm 0.1_5$. We note in passing that if the ultra-centrifuge data of Scholte[20] for polystyrene in cyclohexane are interpreted in terms of M_{os}, then, in the range $0.1 \leqslant \phi_p \leqslant 0.5$ the exponent in the volume fraction dependence is 3.0 at 318 K and 2.6 at 338 K, values which are similar to those reported here.

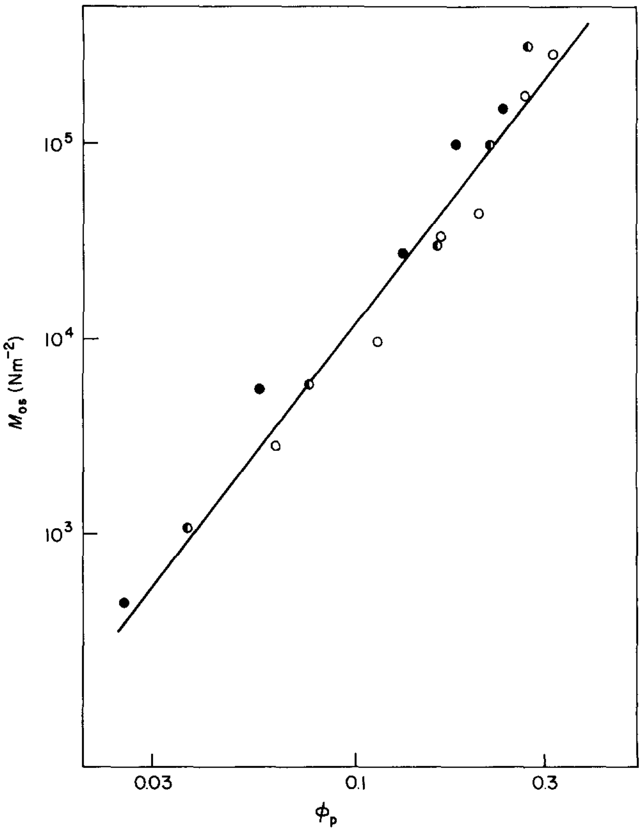

Figure 3 Osmotic modulus, M_{os}, as a function of polymer volume fraction, ϕ_p, for polystyrene networks at swelling equilibrium in cyclohexane. (○) 308 K; (◐) 318 K; (●) 333 K

Cooperative diffusion coefficient D_c

The influence of the measurement temperature is much more evident in the behaviour of D_c than in M_{os}. Part of this difference comes from the temperature dependent factor T/η_s appearing in equation (5), which varies by a factor of 1.5 for cyclohexane between 308 K and 333 K[24].

At 308 K the exponent obtained for $D_c(\phi_p)$ is in agreement with the theoretical theta condition exponent; this result has already been observed in polystyrene *solutions* using classical gradient diffusion techniques[1,2] and QELS[25]. A decrease in the magnitude of the exponent with increasing temperature is also expected as the excluded volume effect becomes stronger. However, the observed value of the exponent, 0.46, at 333 K is much too small to be explained in terms of the finite molecular weight of the polymer coils between crosslink points[26-28]. Although it is not possible to state with certainty the origin of this behaviour, indirect evidence can be obtained from the shape of the QELS spectra. For the more dilute gels, the light scattering spectra become increasingly non-exponential (increasing $\mu_2/\bar{\Gamma}^2$ in equation (4)) as the temperature increases. This behaviour is unusual, in that non-exponential relaxation is more frequently associated with systems containing overlapping coils:[10] here, on the contrary, raising the temperature causes the gels to swell and must therefore decrease coil interpenetration.

It seems probable that, on account of the sample preparation technique used here, the more lightly crosslinked gels contain more voids and dangling chains than the densely crosslinked samples, Such a situation will give rise to non-exponential spectra, and must be considered as a possible cause for the observed departures from scaling behaviour in the more highly swollen samples. In the theta condition, the degree of swelling is small, and there is considerable mutual interpenetration of the coils, so that such defects will not be expected to play a major role. Since the presence of crosslinking defects of this kind influences the hydrodynamic properties more strongly than their osmotic properties, the effect on M_{os} may be rather small. The shear modulus G on the other hand is extremely sensitive to defects of connectivity, and its resulting strong concentration dependence may be sufficient to raise the exponent for M_{os} in good solvent conditions from 2.25 to the value observed here (c.f. equation (2)).

CONCLUSION

For randomly crosslinked polystyrene networks swollen in cyclohexane, the scaling laws obtained for semi-dilute solutions are applicable at the theta temperature of this system.

At temperatures above the theta point, the observed concentration dependence of M_{os} indicates an exponent significantly larger than that theoretically expected, while the observed exponent for D_c is smaller than its theoretical counterpart. These apparent discrepancies may be understood in terms of an increasingly loose structure in the gels as the crosslinking density decreases.

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