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Scaling Analysis of Mechanical and Swelling Properties of Random Polystyrene Networks

R. W. Richards* and N. S. Davidson†

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1X1, United Kingdom. Received September 17, 1985

ABSTRACT: The equilibrium swelling and shear moduli at swelling equilibrium of randomly cross-linked polystyrene gels have been determined in the excluded-volume limit (good solvent conditions), at the Θ temperature, and in intermediate regimes (below and above the Θ temperature). The results have been compared with data obtained by small-angle neutron scattering and quasi-elastic light-scattering measurements on the same gels and discussed by using current analogies between gels and semidilute solutions. An attempt has been made to correlate both macroscopic and molecular behavior in terms of a fundamental thermodynamic correlation length ξ_c, the range of the monomer–monomer pair correlation function. Power law behavior for moduli and diffusion coefficients similar to that which has been reported for semidilute solutions was found in some cases, but departures from simple scaling behavior were also evident. Some of these discrepancies have tentatively been attributed to an increasingly loose structure in the gels as the cross-linking density decreases.

Introduction

Polymeric gels comprising a permanent covalently bound network of long-chain molecules much diluted with a low molecular weight solvent display both elastic and viscoelastic properties.[1,2] They may be regarded either as highly swollen elastomeric solids or as permanently cross-linked solutions of entangled chains. Indeed, when the lifetime of physical entanglements between chains exceeds the time scale of the measurement, the molecular properties of gels and entangled polymer solutions have often been treated as equivalent.[3]

The investigation of macroscopic properties of elastomeric networks such as equilibrium swelling and stress–strain isotherms has been, and continues to be, an area of much effort, being germane to the examination of statistical theories of rubber elasticity. Additionally, the theory of rubber elasticity has a pivotal role in much of polymer science.[4-6] In recent years there has been renewed interest in gels and entangled polymer solutions stimulated by the development of new theoretical and experimental methods. Techniques such as small-angle neutron scattering[2,7-9] (SANS) and photon correlation spectroscopy (PCS)[10-12] have become important as they probe polymer systems on a molecular level, thereby providing data necessary for the rigorous examination of theoretical models. Particular attention has been paid to the analogy between gels and weakly overlapping or semidilute solutions,[3] utilizing the advances in theoretical descriptions of the latter. In spite of considerable progress in our understanding, there are,

however, conflicting experimental data for the global properties of semidilute solutions and no consensus between the theoretical models. Generally the properties in limiting regimes of excluded-volume behavior can be rationalized, but much less well understood is the behavior in situations where the thermodynamic conditions vary over a wide range. Consequently, the situation for true gels is yet more uncertain, as it is compounded by the absence of suitable experimental data.

We report here the results of a series of equilibrium swelling and compressional elastic modulus measurements on randomly cross-linked polystyrene networks covering a range of cross-link density. To study the behavior of the gels under differing thermodynamic conditions, a good (toluene) and a poor diluent (cyclohexane) were chosen as swelling agents. The Θ temperature of polystyrene–cyclohexane systems has been found to be ~35 °C. Consequently the behavior of gels at the excluded-volume limit was studied with polystyrene–toluene gels and at Θ and intermediate conditions (above and below Θ) with polystyrene–cyclohexane gels. The results are compared with the predictions based on the behavior of ξ values obtained from SANS and PCS measurements on the same gels, which we have previously reported elsewhere,[13,14] and are discussed in terms of the analogy with semidilute solutions with the aim of obtaining a viewpoint from which both macroscopic and molecular properties are consistent with each other.

Theoretical Background

The analogy between semidilute polymer solutions and gels swollen by good solvents is embodied in the c^* theorem.[3] Above this critical concentration c^*, polymer mol-

ecules in solution begin to overlap and excluded-volume effects become attenuated. The overlap concentration $c*$ is given by the relation

$$c* \simeq N/R_g^3 \qquad (1)$$

where N is the degree of polymerization of the macromolecules. Since the radius of gyration, R_g, is related to N by the well-known scaling relation

$$R_g \propto N^\nu \qquad (2)$$

where the exponent ν is chiefly determined by the thermodynamic nature of the solvent, we can replace for R_g in eq 1 to obtain

$$c* \sim N^{1-3\nu} \qquad (3)$$

The value of ν was originally determined by Flory as 0.6 for macromolecules at the excluded-volume limit.[4] This value was originally supported by de Gennes[15,16] but has been refined to 0.588 by renormalization group calculations,[17] a value supported by computer simulations.[18,19] Experimentally, however, the difference between the two values is indistinguishable; consequently, we expect

$$c* \sim N^{-0.8} \qquad (4)$$

Above the concentration $c*$ properties of individual molecules (radius of gyration (R_g)) and assemblies of molecules (osmotic pressure and modulus) are describable by universal scaling laws and a fundamental length scale, ξ_c, the correlation length, this being the range of monomer density pair correlations in the solution or gel. In a permanent, covalently bound network of polymer molecules, the swelling in a good solvent brought about by excluded-volume effects is restricted by the cross-links or junctions, which impose a permanence of structure on the whole assembly by engendering an elastic restoring force in the swollen macromolecules. The equilibrium concentration of polymer in the gel, c_e, is proportional to $c*$

$$c_e = k(f)c* \qquad (5)$$

where $k(f)$ is a constant determined primarily by the junction functionality, f. From eq 4 we have

$$c_e \sim N_c^{-0.8} \qquad (6)$$

where N_c is the degree of polymerization between cross-links. Essentially eq 5 is a generalization of the well-known Flory-Rehner equation[4] for the equilibrium swelling of networks. As a consequence of eq 5, it is expected that the scaling laws pertaining to semidilute solutions should also be found for gels.

These scaling laws and in particular the correlation length, ξ_c, have been discussed in an earlier paper.[13] Physically, ξ_c is a measure of the effective screening of interactions between monomers.[20-22] For length scales smaller than ξ_c intramolecular interactions (excluded-volume effects) determine the configurational statistics; at greater length scales it is the intermolecular effects that dominate. Essentially, the chain is a series of "blobs" of diameter ξ_c. For gels the blob picture is still applicable in that the gel can be viewed as an assembly of close-packed correlation spheres with diameter ξ_c. The fundamental scaling for ξ_c is

$$\xi_c \sim c^{-m} \qquad (7)$$

where $m = \nu/(3\nu - 1)$ and for good solvent conditions $m = 0.75$. Scaling laws are an attempt to account for excluded-volume correlations in polymer solutions that were neglected by early mean field theories[4] (whether of fifth

power or cubic type), and strictly they are only applicable to infinite molecular weight polymers subjected to strong excluded-volume effects. However, scaling laws for other regimes of polymer solution behavior have been obtained, and "phase diagrams" of polymer solution behavior have been evolved;[23] in particular a regime of weak excluded-volume behavior is predicted wherein m in eq 7 is 0.5. In this region the correlation length reflects screening due to ternary interactions,[24] since binary interactions disappear under Θ conditions. By contrast, in the true Θ condition where excluded-volume behavior is absent, the value of m is expected to be 1.0. The original development of scaling laws was based on the renormalization group theory of magnetic systems developed by Wilson.[25] Somewhat preceding this development, Edwards[20,26,27] had used the mean field theory to analyze the properties of concentrated polymer solutions. This theory has been developed further into a renormalized mean field theory[28] with single formulas for ξ_c and radius of gyration that extrapolate between dilute solutions and bulk polymer in the presence or absence of strong excluded-volume effects and are able to reproduce all the predictions of the original scaling laws. Although this mean field theory can account for the different exponents obtained by techniques such as SANS and PCS,[21,22,29-32] Schaefer[24,26] has attempted to attribute such variations to the breakdown of simple scaling caused by the stiffness of real chains.

All the scaling laws and their exponents alluded to above should be directly applicable without modification to highly swollen permanent networks, i.e., gels, according to eq 5. A direct test is the examination of ξ_c in gels swollen to equilibrium under different thermodynamic conditions; such an examination has been reported by us earlier.[13] However, a complete evaluation of the applicability of scaling laws requires an investigation of the relation between the elastic moduli and ξ_c. Classically, the elastic properties of swollen networks have been interpreted by using the statistical theory of rubberlike elasticity modified for polymer–solvent interactions by the original Flory mean field theory of polymer solutions.[4-6] Rigorously, this will be incorrect due to the neglect of excluded-volume correlations referred to earlier. The scaling concepts can be extended to the elastic properties to yield scaling relations between a modulus (E) and ξ_c. The elastic modulus is proportional to the number density of junctions, n_e[33-35]

$$E \sim n_e \simeq (c_e/N_c)k_BT \qquad (8)$$

where N_c is the degree of polymerization between cross-links, k_B the Boltzmann constant, and T the absolute temperature. When the $c*$ theorem is used, N_c may be replaced for in terms of c_e

$$E \simeq c_e^{3m}k_BT \qquad (9)$$

and utilizing eq 7 (which implicitly presumes that the mesh size of the network is proportional to, if not equal to, ξ_c)

$$E \sim k_BT/\xi_c^3 \qquad (10)$$

Equation 9 thus predicts that the modulus for networks swollen in good solvents scales with the equilibrium concentration of polymer to the power 2.25. Furthermore, eq 9 and 10 are applicable to *any* elastic modulus of the network (bulk or shear). Deformation of an elastic solid may be represented as the sum of a pure shear and a hydrostatic compression.[36] Pure shear corresponds to a distortion of the elastomer without alteration in volume; it is characterized by the shear modulus, G, which is formally defined in terms of the elastic free energy, A, as

$$G = [\partial A/\partial(\Lambda - \Lambda^{-2})]/(\Lambda - \Lambda^{-2}) \qquad (11)$$

Table I
Exponents for the Limiting Power Law Dependence of Various Gel Properties on Polymer Concentration in the Region of Overlapping Chains

	strong excluded volume	weak excluded volume	random flight Θ state
range of monomer pair correlation, ξ_c	−0.75	−0.5	−1.0
cooperative diffusion coefficient, D_c	+0.75	+0.5	+1.0
shear modulus, G	+2.25	+2.0	+3.0
longitudinal osmotic modulus, M_{os}	+2.25	+2.0	+3.0

where Λ is the ratio of deformed to undeformed dimensions. Hydrostatic compression is accompanied by a change in volume of the elastomer without any change in specimen geometry; the compressional modulus, K, is the characteristic parameter for this situation and

$$K = \rho(\partial\Pi/\partial\rho)_T \qquad (12)$$

where ρ is the network density and Π the compressional pressure. For networks swollen by solvent there is a second compressional modulus of interest, the osmotic compressional modulus,[37] K_{os}, arising from the polymer network moving independently of the swelling fluid. Equation 12 also defines K_{os}, but ρ is replaced by the concentration of polymer, c, and Π by the osmotic pressure, Π_{os}, of the gel. For elastomers the ratio G/K is usually small; however, K_{os} is several orders of magnitude smaller than K.

Shear moduli, G, can be most directly evaluated by simple stress–strain measurement; for gels, their mechanical weakness necessitates compressional loading rather than elongational loading. Additionally a value of G can be deduced from the equilibrium swelling of a gel, since this pertains to the situation at which osmotic swelling and retractive elastic restoring forces balance each other. Values of compressional moduli have been determined by noting the decrease in equilibrium swelling of gels in polymer solutions[38,39] or when under an external load.[40,41] The longitudinal osmotic modulus, M_{os}, is a combination of G and K_{os}

$$M_{os} = K_{os} + (4/3)G \qquad (13)$$

and may be obtained from the intensity of light scattered by nonpropagating collective excitations of the gel.[42] These collective excitations are also observable as an autocorrelation function of the elastically scattered light, from the relaxation time of which a cooperative diffusion coefficient, D_c, can be obtained. This diffusion coefficient can be related directly to the correlation length if the Stokes–Einstein equation is applicable to the correlation spheres of the network[33,34]

$$D_c \sim k_B T/6\pi\xi_c\eta_s \qquad (14)$$

where η_s is the solvent viscosity in the gel. If the analogy between semidilute solutions and gels holds and the phase diagram of solution behavior is also applicable, a series of scaling laws for each of the properties of the gel (moduli, correlation length, and cooperative diffusion coefficient) can be written in terms of the equilibrium polymer concentration of the network; exponents are reproduced in Table I for the three major areas of the solution behavior diagram.

Experimental Section

Network Preparation. Linear, atactic polystyrene with a weight-average molar mass of $\sim10^5$ Da, as determined by gel permeation chromatography, was synthesized by anionic polymerization in tetrahydrofuran solution. Polystyrene disks, 13 mm in diameter and between approximately 1 and 10 mm in height, were prepared by compression molding the linear polymer in an evacuable die, followed by heating to 450 K and cooling below the glass transition temperature while in the press. The disks were placed in glass ampules that were then evacuated and flame sealed. The samples were subsequently randomly cross-linked by irradiation[43] at ambient temperature in a ^{60}Co source at a dose rate of 5 kGy h^{-1} to total doses between 2 MGy, nominally the gel point dose for polystyrene of molecular weight 10^5, and 10 MGy. After irradiation, sol fraction was removed by exhaustive extraction, first in cyclohexane and then in toluene. The gels were then carefully deswollen and thoroughly dried, so that the weight of polymer network could be measured.

In the experiments reported here, two series of networks corresponding to different precursor linear polystyrene were used. The N1 series was prepared from a narrow distribution sample, $M_w = 8.4 \times 10^4$ and $M_w/M_n = 1.05$, and the B2 series from a sample with a broader distribution, $M_w = 1.62 \times 10^5$ and $M_w/M_n = 1.73$.

Swelling Measurements. The dry extracted networks were swollen to equilibrium in cyclohexane at four different temperatures in the range 298–333 K and also in toluene at ambient temperature, 293 K.

The degree of swelling was determined by a weighing method,[44] and in calculating the volumetric swelling it was assumed that the specific volumes of the solvent and polymer were additive. Values of the specific volume of polystyrene in networks in bulk and in good and poor solvents were taken from the data of Sarazin et al.,[45] assuming specific volume to be independent of polymer concentration and molar mass over the range of gel volume fraction and cross-link density explored. The equilibrium swelling was determined by weighing the gels periodically until an essentially constant weight was attained. This required from several hours to several weeks, depending on the dimensions of the dry network specimen, the initial degree of swelling of the gel, and the cross-link density.[44]

Mechanical Measurements. Unidirectional compression measurements were performed on gels swollen to equilibrium in toluene at 293 K and in cyclohexane at 298, 303, 318, and 333 K. The equilibrium-swollen samples were held at the temperature of measurement for at least 1 week prior to compression measurements, and the value of the equilibrium swelling was determined for each individual gel sample used.

The stress–strain isotherms were measured by using an apparatus[44] that is essentially a development of one which has previously been described by Fasina and Stepto.[46] Briefly, a load is transmitted vertically to the gel by a piston freely suspended from a converted knife-edge analytical balance, and the resultant deformation is measured by a linear-displacement transducer with the output displayed on a digital voltmeter. The swollen gel under test, surrounded by an excess of solvent, was contained in a flat-bottomed jacketed glass beaker whose temperature was maintained to within ±2 °C of the desired temperature by circulating water. Initial experiments were performed to estimate corrections for buoyancy effects on the piston in the solvent and to evaluate the capabilities of the apparatus. Summarizing the results of these tests, we found that the apparatus could reliably respond to forces down to 0.005 N and measure deformations of 0.004 mm. This is comparable with a similar apparatus described by Horkay et al.[47]

Cylindrical specimens of 10-mm diameter and 10-mm height, cut from larger swollen gels, were found suitable for measurement in this apparatus. The undistorted dimensions were measured by using a traveling microscope, and, as it was difficult to cut perfect cylindrical samples from the swollen gels, the average dimensions were determined from several measurements for each specimen. A serious problem that had restricted the application of compression measurements on elastomers is the friction which occurs between the elastomer and surfaces in contact with it.[48] This friction interferes with the uniform expansion of the elastomer at these contact surfaces, and the sample exhibits nonuniform expansion (i.e., "barreling") in the direction perpendicular to the compression direction, which is indicative of inhomogeneous stress distribution. This surface–elastomer friction was eliminated in our measurements by placing the gel between two thin Teflon

sheets during compression. Under these conditions our samples did not exhibit any significant barreling effect.

For swollen gels under an external load, thermodynamics predicts that the gel will deswell.[5] The rate of diffusion is such that this ought not to be serious if the test is carried out fairly rapidly. An additional problem is the rate at which elastic equilibrium is attained after application of the load; however, this is believed to be almost instantaneous in highly swollen networks under moderate deformations. A typical determination of a stress–strain isotherm involved about 20 measurements of displacement as a function of load covering the range up to ~25% compression and was completed within 30 min.

The data were routinely analyzed according to the two-constant phenomenological theory of rubber elasticity of Mooney and Rivlin,[5,49–51] which for uniaxial deformation yields the equation

$$\sigma = 2C_1(\Lambda - \Lambda^{-2}) + 2C_2(\Lambda - \Lambda^{-2})\Lambda^{-1} \tag{15}$$

σ is the applied stress

$$\sigma = F/A \tag{16}$$

F being the applied load and A the undeformed (swollen) cross-sectional area. Λ is the deformation ratio, given by

$$\Lambda = (l_0 - \Delta l)/l_0 \tag{17}$$

where l_0 is the undeformed length and Δl is the change in length caused by the applied load. The interpretation of constants $2C_1$ and $2C_2$ has not been clearly established, but the experimental dependencies and suggested interpretations of these constants have been reviewed.[51] Since $2C_1$ depends primarily on cross-link density, it has been equated in most cases with the elastic modulus, G. Statistical theories of rubber elasticity of Gaussian chains derive an equation of the form

$$\sigma = G(\Lambda - \Lambda^{-2}) \tag{18}$$

for the stress in uniaxial deformation, so C_2 has served as a measure of the departure of the observed stress–strain relation from the predictions of statistical theories. The general interpretation of Mooney–Rivlin plots (i.e., $\sigma/(\Lambda - \Lambda^{-2})$ against Λ^{-1}) is that $2C_1$ corresponds to the high-deformation limit in elongation, $(2C_1 + 2C_2)$ corresponds to the low-deformation elongation modulus or the compressional modulus, and $2C_2/2C_1$ reflects departures from the Gaussian theories of rubber elasticity without specifying the source of these deviations.

Results

Swelling Measurements. Reproducibility of the equilibrium swelling was evaluated by comparison of several networks prepared from the same linear precursor polymer and that had received nominally the same dose. The relative standard deviation of the equilibrium swelling was worst in networks that had received doses just above the gel point and was as high as 25%, but this standard deviation rapidly decreased with increasing dose to an average value of ~5%.

As anticipated, in a given solvent the degree of swelling decreased with increasing radiation dose, i.e., increasing cross-link density. Figure 1 shows the polymer volume fraction at swelling equilibrium in toluene as a function of radiation dose for the two series of networks. The solid curves serve merely to illustrate the trend and have no other significance, but extrapolation to zero volume fraction (i.e., infinite swelling) enables the gel point dose to be estimated. In accord with the molecular weights of the linear precursor polymers, the gel point dose for the B2 series networks, prepared from the higher molecular weight polymer, was lower than for the N1 series. Consequently for a given dose above the gel point the B2 series is more highly cross-linked than the N1 series. Following the scaling law approach, it is instructive to display the data logarithmically. This is shown in Figure 2 with the radiation dose (D') expressed in a reduced form with respect
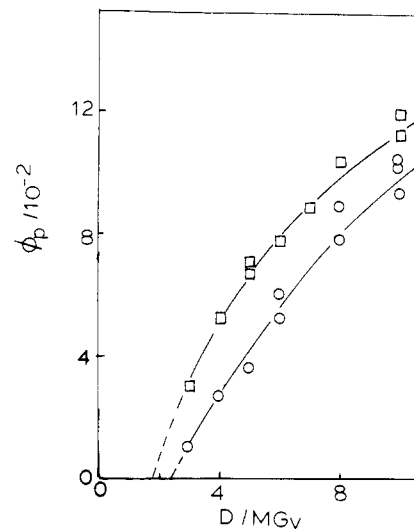

Figure 1. Volume fraction of polymer, ϕ_p, for gels at swelling equilibrium in toluene at 293 K as a function of radiation dose D: (O) N1 series; (□) B2 series.
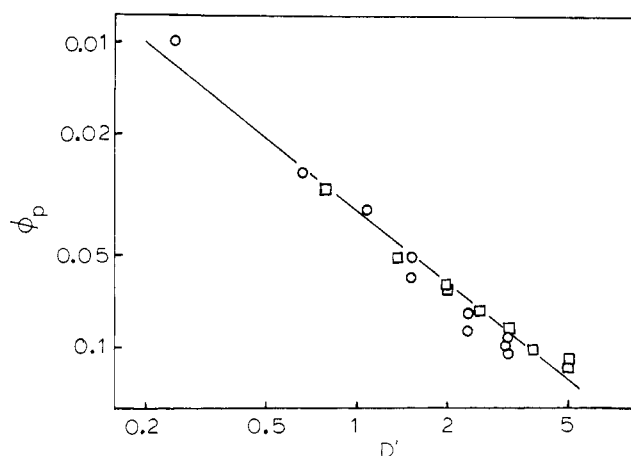

Figure 2. Polymer volume fraction at swelling equilibrium in toluene as a function of the reduced dose D': (O) N1 series; (□) B2 series.

to the gel point dose (D_g) obtained from the extrapolation of the curves in Figure 1.

$$D' = (D - D_g)/D_g \tag{19}$$

Both sets of data can be described by a single line with a slope of ~−0.8 (eq 6). This exponent is in agreement with the c^* theorem for the dependence of equilibrium swelling in a good solvent on the molecular weight between cross-links. For these two series of networks, prepared under the same conditions, the equilibrium swelling in the same solvent is directly related to the cross-link density, which in turn depends on the radiation dose normalized with respect to the gel dose.

The degree of swelling of the networks in cyclohexane, a poor solvent for polystyrene, was less than in toluene, as expected. At moderate temperatures the solvent power of cyclohexane for polystyrene increases with increasing temperature, and consequently the swelling of the networks increased. However, even at the highest temperature investigated, 333 K, the swelling was much less than in toluene at ambient temperature. As for toluene, the degree of swelling in cyclohexane decreased with increasing radiation dose. The data could again be conveniently displayed on a double-logarithmic plot of equilibrium volume fraction against reduced radiation dose (Figure 3).
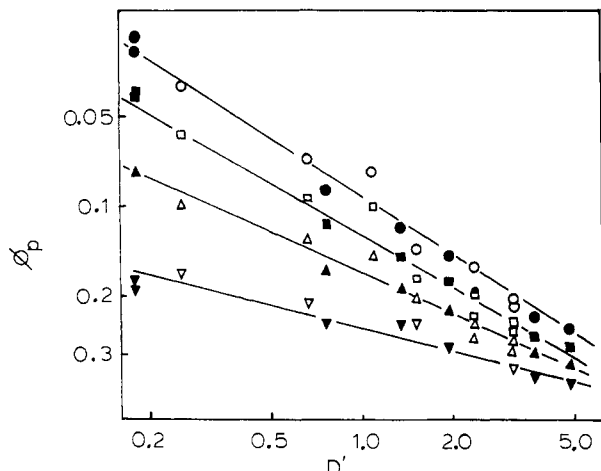
Figure 3. Polymer volume fraction at swelling equilibrium in cyclohexane at a variety of temperatures as a function of reduced dose D': ($\bullet$, $\bigcirc$) 333 K; ($\blacksquare$, $\square$) 318 K; ($\blacktriangle$, $\triangle$) 308 K; ($\blacktriangledown$, $\triangledown$) 298 K.
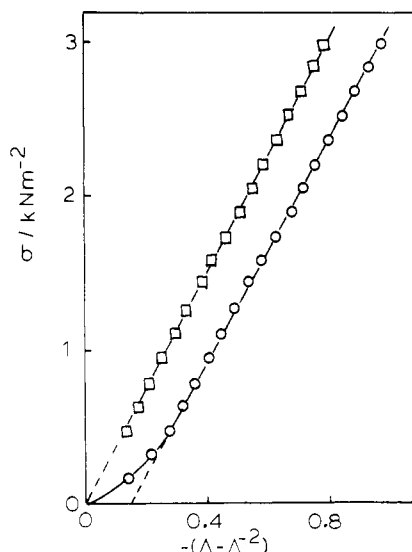

Figure 4. Typical stress, σ, vs. deformation plot for a gel at swelling equilibrium in cyclohexane at 333 K: ($\bigcirc$) uncorrected data; ($\square$) data corrected for nonplanar effects at the surface.

At each temperature both series of networks could be described by a single line. The magnitude of the slope increased with improved solvent quality from $\sim$0.25 at 298 K to $\sim$0.65 at 333 K. At 308 K the slope of -0.5 may be explained by the application of the c^* theorem to unperturbed random coils (i.e., the Θ condition), but at the other temperatures the exponent is empirical and has no known theoretical significance. One can only speculate as to whether below Θ it reflects a transition to a regime of collapsed coils and above Θ a crossover leading eventually to a regime of strong excluded-volume behavior.

Mechanical Measurements. A typical set of stress–strain data correlated according to the classical Gaussian theories of rubber elasticity, eq 18, is shown in Figure 4. In the region of small deformations there is an obvious discrepancy from the anticipated linear relationship. Departures from Gaussian theory have almost invariably been treated with the full Mooney–Rivlin expression (eq 15), but Figure 5 shows that the data do not conform to this correlation either.

Similar deviations from the form of the statistical theories at low deformations have been reported in the literature. In the main, these deviations have been attributed to slight imperfections in the geometry of the sample and
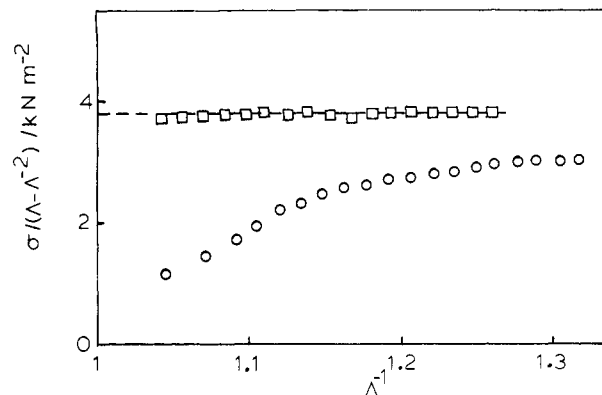

Figure 5. Mooney–Rivlin plot for the data of Figure 4. Different symbols have the same significance.

compressing plates,[52,53] but recently there has been an attempt to correlate such behavior with molecular structure of the network.[46,54] According to this latter analysis, the low-strain departures from linearity could not be accounted for by a correction to the initial length to allow for surface roughness and, furthermore, the effect diminished with increasing molecular weight between cross-links. Therefore, the nonlinearity was subsequently interpreted as indicative of a non-Gaussian distribution of the end-to-end vectors of the network chains due to finite chain length between junctions. In the measurements made here, however, data in the low-deformation region were subject to considerable error and were not generally reproducible. Indeed, no trend could be found between the size of the deviations and cross-link density or the degree of swelling. Consequently, it was believed it would have been placing too much emphasis on unreliable low-strain data to have interpreted these deviations as strictly due to non-Gaussian behavior and they could best be accounted for by surface unevenness on the samples and compressing plates.

Surface nonuniformity will mean that the area subject to the load is less than that calculated from the mean diameter of the sample, and as a result, the effective stress is enhanced at the initial low-strain deformations. To account for these sample imperfections the stress–strain isotherm was corrected by discarding the data at very low strains by extrapolating back from the linear portion of the curve in Figure 4 to a value of $-(\Lambda - \Lambda^{-2})$ for $-\sigma = 0$ where it was assumed that the cross-sectional area was that measured. The corrected initial length was computed from this value of $-(\Lambda - \Lambda^{-2})$, and the deformation ratios were suitably adjusted; data corrected in this manner are also shown in Figures 4 and 5. The correction to the undeformed length was, on average, $\sim$3%. The dramatic transformation of the data by this small correction is best seen in the full Mooney–Rivlin plot, and it was generally found that over the moderate deformation range $1.05 <$ $\Lambda^{-1} < 1.35$ the simple Gaussian form was obeyed; i.e., $2C_2$ was zero within experimental error. This finding is in agreement with many reported studies of rubber networks in uniaxial compression that have shown stress–strain relationships which exhibit only small deviations at moderate deformations from the form predicted by statistical theories of rubber elasticity. In particular two important features of the Mooney–Rivlin plot relevant to this type of study have been reported: (1) the value of $2C_2$ is considerably reduced for a material measured in compression compared to elongation, and (2) the value of $2C_2$ is reduced for swollen networks compared to bulk networks and is essentially zero for a polymer volume fraction less than 0.25. The constant $2C_1$ was subsequently interpreted as the elastic modulus of the networks. Many reported
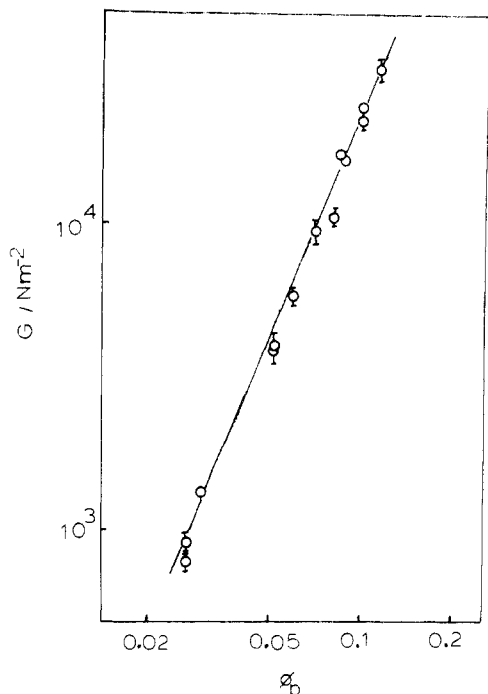
Figure 6. Double-logarithmic plot of shear modulus, G, as a function of polymer volume fraction, ϕ_p, for gels at swelling equilibrium in toluene at 293 K.

studies of the compressional modulus of gels are in concurrence with this finding.[48,52,53] By way of a final comment on the shape of the measured stress–strain isotherms, a recent development of the classical theories of rubber elasticity by Flory and Erman[65,66] taking account of constraints of junction fluctuations in real networks compared to model phantom networks[67,68] does actually predict curvature of the reduced stress–strain plot in compression but at larger deformations than measured here; moreover, the effect is diminished on decreasing the polymer volume fraction in the gel by swelling in a diluent.

The reproducibility of the compression measurements on the swollen gels was assessed in three ways. First, samples were tested in loading and unloading, and allowing for uncertainty in the undeformed dimensions, no significant hysteresis was measurable. For each network specimen compression measurements were made at least three times over a period of several days; furthermore, samples cut from different regions of the same gel were also measured. Within the limits of experimental uncertainty on the measured stress–strain isotherm for one sample, no difference was found between specimens cut from the same gel, the overall reproducibility being limited by the quality of the individual samples and was ~5–10%.

The elastic shear modulus was calculated in three ways from the stress–strain data: (1) from the slope of the linear part of the curve for the unshifted data, (2) from the slope of the linear correlation of the corrected data, and (3) from the intercept $\Lambda^{-1} = 1$ (i.e., the constant $2C_1 + 2C_2$) of the full Mooney–Rivlin treatment; no difference between the values obtained by the different methods was noted. The shear modulus for the different networks was subsequently correlated with the equilibrium polymer volume fraction following the scaling approach on a double-logarithmic plot. Figure 6 shows the data obtained for the gels swollen in toluene at 293 K, and the data for the gels in cyclohexane at 298, 308, 318, and 333 K are presented in Figure 7. In each case the experimental points are described by a unique curve irrespective of the polystyrene molecular
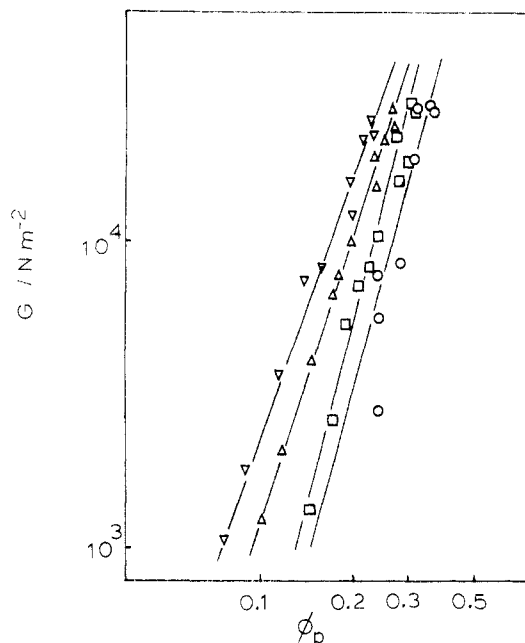

Figure 7. Double-logarithmic plot of shear modulus as a function of volume fraction for gels at swelling equilibrium in cyclohexane at different temperatures: (O) 298 K; (□) 308 K; (△) 318 K; (▽) 333 K.

weight or distribution prior to cross-linking. Linear regression gives the best-fit curve for the gels in toluene as

$$G/(\mathrm{N\ m^{-2}}) = (5.37 \pm 0.25) \times 10^6 \phi_p^{2.39 \pm 0.02} \quad (20)$$

and for the gels in cyclohexane

298 K:
$$G/(\mathrm{N\ m^{-2}}) = (1.23 \pm 0.18) \times 10^6 \phi_p^{3.65 \pm 0.10}$$
$$(21)$$

308 K:
$$G/(\mathrm{N\ m^{-2}}) = (2.24 \pm 0.10) \times 10^6 \phi_p^{3.71 \pm 0.03}$$
$$(22)$$

318 K:
$$G/(\mathrm{N\ m^{-2}}) = (1.41 \pm 0.1) \times 10^6 \phi_p^{3.04 \pm 0.05}$$
$$(23)$$

333 K:
$$G/(\mathrm{N\ m^{-2}}) = (1.51 \pm 0.1) \times 10^6 \phi_p^{2.79 \pm 0.04}$$
$$(24)$$

Error limits are the standard errors obtained from linear regression. The magnitudes of the measured moduli are in reasonable agreement with published data for polystyrene–benzene gels[58] and for polystyrene–cyclohexane solutions.[69] Furthermore, the intercept at a polymer volume fraction of unity is of the same order of magnitude as reported for the plateau modulus of bulk polystyrene,[70] ~2 × 10^6 N m^{-2}.

Discussion

In all the swelling and mechanical measurements reported here the data for given conditions could be described by a single curve with no apparent indication of any concentration crossover or artifact of cross-linking density, so that, to a first approximation, invoking the C^* theorem and scaling analysis seems justifiable. The power law dependence of the shear modulus has been deduced from the experimentally determined scaling behavior of the equilibrium swelling by using eq 6, assuming N_c to be proportional to the reduced radiation dose, in eq 8. The results are reported in Table II as are the exponents of the concentration dependence of the modulus determined directly in mechanical compression testing. Both series of measurements exhibit the same trend: the apparent exponent decreases with increasing solvent quality. The behavior is qualitatively in agreement with a recent com-

Table II
Summary of Experimentally Determined Scaling Exponents for the Concentration Dependence of Some Properties of Random Polystyrene Networks at Swelling Equilibrium

conditions	measured scaling exponents				
	$G(c)^a$	$G(c)^b$	$M_{os}(c)^c$	$\xi(c)^d$	$D_c(c)^e$
cyclohexane, 298 K	5.35	3.65			
cyclohexane, 308 K	3.27	3.71	2.94	−0.85	1.17
cyclohexane, 318 K	2.72	3.04	2.62	−0.67	0.67
cyclohexane, 333 K	2.54	2.79	2.62	−0.56	0.46
toluene, 293 K	2.25	2.39		−0.5/−0.75	

^{a} Equilibrium swelling measurements (this work). ^{b} Mechanical compression measurements (this work). ^{c} Light-scattering intensity measurements (ref 14). ^{d} Small-angle neutron scattering (ref 13). ^{e} Measurement of the autocorrelation function of scattered light (ref 14).

prehensive study of poly(vinyl acetate) gels over a wide range of swelling conditions.[71] In the polystyrene–toluene gels (good solvent conditions) the exponent approached the limiting value for strong excluded volume of 2.25 predicted by scaling theory. In the polystyrene–cyclohexane gels the apparent exponent decreased with increasing temperature (increasing solvent quality). At the Θ condition, 308 K, the predicted exponent is 3, but the experimental data obtained for these gels indicate a stronger dependence. At the highest temperature investigated here, 333 K, although the exponent has decreased, it has not reached the good solvent limit. This is understandable since the equilibrium degree of swelling in cyclohexane at 333 K is much less than in toluene, which may be taken as a macroscopic symptom of the fact that excluded volume in individual macromolecular coils is smaller in cyclohexane. It should be noted that while it is tempting to regard this situation as that of the marginal solvent regime, the measured power law exponent considerably exceeds the mean field value of 2. Below the Θ temperature the exponent continues to increase, as has been noted by other workers[71] and attributed to a transition to a region of collapsed coils.

To evaluate the significance of these results in terms of scaling theory it is germane to compare them with SANS and PCS results obtained for the same gels. To this end the power law exponents for the concentration dependence of M_{os}, D_c, and ξ_c are also included in Table II. The experimental details of the measurements of these latter parameters have been reported previously.[13,14]

The exponent for the concentration dependence of M_{os} for polystyrene–cyclohexane gels is in moderate agreement with the Θ prediction of 308 K, but although reduced at higher temperatures, it remains considerably greater than the good solvent or marginal solvent limiting values. The concentration dependence of M_{os} is notably weaker than the corresponding behavior of G.

In passing it is interesting to compare our data on polystyrene gels with the ultracentrifugation data of Scholte[72] for polystyrene solutions interpreted in terms of M_{os}. Figure 8 for polystyrene in cyclohexane and Figure 9 for polystyrene in toluene show that the exponent varies continuously over the entire concentration range from 1% up to bulk polymer. However, the limiting values of the exponents over the concentration range corresponding to that covered by the gels used here are in remarkable agreement with our values obtained for the gels.

Turning to the cooperative diffusion coefficient, we see that the power law exponent for the concentration dependence for polystyrene–cyclohexane gels at 308 K is also in accord with the Θ prediction, but at higher temperatures
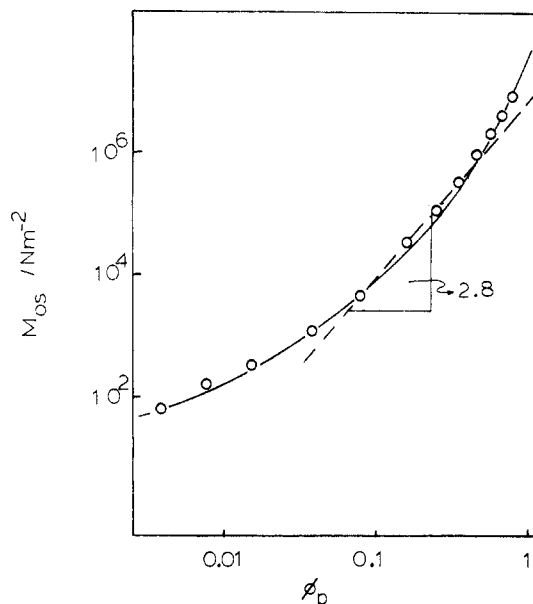

Figure 8. Osmotic modulus, M_{os}, as a function of volume fraction of polystyrene in cyclohexane solution at 318 K. Data from the work of Scholte.[72]
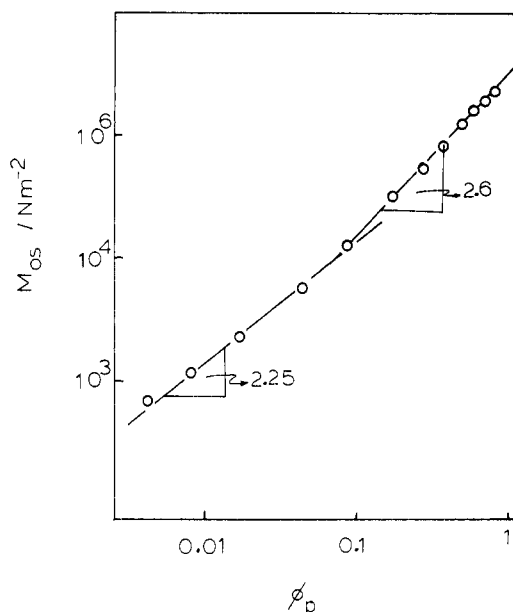

Figure 9. Osmotic modulus as a function of polystyrene volume fraction in toluene solution at 298 K. Data from the work of Scholte.[72]

it is much reduced and falls below the limiting value for the semidilute good solvent regime.

Finally the behavior of the correlation length measured directly by SANS has been included since the elastic moduli and the diffusion coefficient are expected to be related to ξ_c through the scaling relations of eq 10 and 14. In the polystyrene–toluene gels we noticed a concentration crossover in ξ_c that does not appear in any of our other data wherein ξ_c would be expected to play a role according to scaling law ideas. At the lowest polymer concentration the exponent corresponds to the scaling limit of 0.75, while at higher concentrations it was closer to the Edwards value of 0.5. As far as we are aware, such a concentration crossover has not been reported for direct measurements of ξ_c in semidilute solutions, although evidence for good and marginal behavior has been obtained for different systems. The osmotic modulus data of Scholte for polystyrene–toluene solutions (Figure 9) may, however, be

construed to show a crossover around a polymer volume fraction of 0.1. Only at the lowest polymer concentrations are the scaling exponents of ξ_c and the elastic moduli compatible with eq 9 for the polystyrene gels. At higher concentrations the correlation between ξ_c and C weakens, but this is not reflected in the behavior of the shear modulus, which still corresponds to the good solvent limit. In the case of the polystyrene–cyclohexane gels the scaling exponent of ξ_c at the Θ condition is again in modest concurrence with theory, as found for the exponents of M_{os} and D_c but not for G. The scaling relations of ξ_c with M_{os} and D_c in eq 10 and 14 seem to be justified. At higher temperatures the concentration dependence of ξ_c for the polystyrene–cyclohexane gels weakens and the exponent falls below the good solvent limit and at 333 K is close to the Edwards limiting value for m of 0.5. The concentration dependence of ξ_c and D_c for the polystyrene–cyclohexane gels is consistent with eq 14, but the behavior of ξ_c and the elastic moduli (M_{os} and G) are not in concurrence with eq 10.

It is clear that the structure of these permanent gels is to some extent modifying the scaling behavior from the predicted by the c^* theorem and the scaling laws for semidilute solutions. In these gels the concentration for given equilibrium swelling conditions is controlled by the cross-link density: at low equilibrium concentrations the cross-link density is low and the mesh size is correspondingly large, whereas higher concentrations are achieved by increasing the cross-link density and reducing the mesh size. In view of the random cross-linking technique employed in the sample preparation, it is conceivable that the properties of the more lightly cross-linked gels are more prone to the influence of defects such as nonuniform cross-link density and dangling chains than the more highly cross-linked samples. The shear modulus would be expected to be extremely sensitive to defects of network connectivity, and indeed this seems to be supported by the strong concentration dependence of the equilibrium swelling and mechanical measurements reported here for the polystyrene–cyclohexane gels. We have previously argued[14] that since Θ coils interpenetrate to a greater extent than those with excluded volume the influence of the defects would increase as the solvent quality improved, but this appears to be contradicted by the behavior of the shear modulus shown in Table II. Is seems rather as if the chains with excluded volume are less subject to catastrophic failure due to network defects.

Bastide et al.[73] have carried out an investigation into the effect of the fraction of pendant chains in model polystyrene networks. They observed that neither the equilibrium swelling nor the cooperative diffusion coefficient was much affected by small fractions of pendant chains, but the shear modulus was strongly reduced. This behavior was rationalized by considering D_c and C_e to be related to ξ_c, which was largely unaffected by pendant chains, whereas G was considered proportional to the number of elastically effective chains, which was quite sensitive to the fraction of dangling chain ends. They concluded that there is no simple relation between the elastic modulus and the equilibrium concentration in general, and therefore any scaling behavior observed in gels may be purely fortuitous.

This description is certainly in qualitative agreement with the observed behavior in these random polystyrene networks swollen by poor solvents, but does not then account for the better agreement with theory in good solvents. One might care to surmise that as the solvent quality improves and the chains are expanded by exclud-

Table III
Shear Moduli (N m⁻² K⁻¹) for Gels at Swelling Equilibrium in Cyclohexane, Normalized by $\phi_p^{1/3}$ and Temperature

dose, MGy	temp, K			
	298	308	318	333
	Series N1			
5		8.4	8.2	7.6
6	42	40	38	35
8		109	96	81
8		54	54	46
10	134	110	106	109
10	92	78	77	63
	Series B2			
3	15	15	14	12
4	30	31	24	23
5	43	44	44	38
8	140	136	134	124
10	127	124	117	109

ed-volume effects, dangling chains and branches are more able to form supplementary cross-links by discrete entanglements with other network chains. This hypothesis may be tested by normalizing the shear moduli to a reference state, conveniently the bulk state, i.e., zero swelling. Since the shear modulus should be proportional to the concentration of elastically effective chains, the normalized moduli should reflect any change due to discrete entanglements described above. The results shown in Table III, however, do not unambiguously confirm this conjecture, since the variation in G is within experimental error. Militating against this hypothesis is the fact that polymers in good solvents usually behave as hard spheres and do not interpenetrate.

In the system studied here the influence of pendant chains would be expected to be greatest at low cross-link density where the ratio of pendant chains to elastically effective chains is greatest. The concentration dependence is certainly weakened for gels in cyclohexane at 298 and 308 K if we neglect the results obtained for gels with lowest cross-link density. The strength of this effect is, however, reduced in better quality solvent conditions. We can only conclude at this stage that if pendant chains do perturb scaling behavior, the observable effect diminishes as the solvent quality improves.

As a postscript to this discussion it should be pointed out that no mention has been made of the possible influence of large-scale inhomogeneities (e.g., aggregations of chains, clustering of junctions, or microscopic phase separations) on the elastic response as reflected in the scaling behavior. There is no real theoretical or experimental understanding of such features yet. One could imagine two simple possibilities: chain clusters acting as filler particles and strengthening the material *or* the primary effect of clustering of chains being evidenced by a reduction of the volume fraction of gel occupied by elastically active chains and so perturbing the measured power law. The question of large-scale heterogeneities has been more fully discussed in a recent paper by Nagy.[74]

Conclusion

The concentration dependence of the equilibrium elastic modulus of random polystyrene networks inferred from equilibrium swelling and uniaxial compression measurements could be described by empirical power laws. Comparison of the macroscopic behavior with SANS and PCS data provides some support for the c^* theorem, but several discrepancies exist. In some instances deviations from theoretical predictions for the power law behavior of the elastic response of the gels may reflect defects in the network structure arising in the sample preparation. The

behavior of the gels in the excluded-volume limit and at the Θ temperature, conditions where scaling analysis is expected to be valid, provide the best agreement with theory. At intermediate swelling conditions where there is believed to be a breakdown of simple scaling, the concentration dependence of ξ_c and D_c seem consistent, the power law exponent lying close to Edwards' weak excluded-volume limiting value, but the concentration dependence of the elastic model considerably exceeds the mean field prediction. It may be necessary to postulate further characteristic length scales to obtain a comprehensive model of polymer gels to include the regime of intermediate swelling behavior.

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