Scattering Properties of Poly(vinyl acetate) Gels in Different Solvents

Ferenc Horkay,[*,†,‡] **Walther Burchard,**[†] **Anne-Marie Hecht,**[§] **and Erik Geissler**[§]

Institut für Makromolekulare Chemie, Universität Freiburg, Stefan Meier Strasse 31,
D-7800 Freiburg i.Brsg., FRG, Department of Colloid Science, Eötvös Loránd University,
Pázmány Péter sétány 2 Pf. 32, H-1518 Budapest, Hungary, and Laboratoire de
Spectrométrie Physique,[∥] *Université Joseph Fourier de Grenoble,*
B.P. 87, F-38402 St. Martin d'Hères, France

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ABSTRACT: The thermodynamic properties of lightly cross-linked PVAc gels swollen in different solvents (acetone at 25 °C, isopropyl alcohol at 70 °C, isopropyl alcohol at 52 °C) are investigated by osmotic and scattering techniques. The first two diluents are good solvents, and the last is a Θ solvent. The relaxation rates of the concentration fluctuations, measured by dynamic light scattering, are greater in the gels than in the corresponding solutions. In all cases, however, the longitudinal osmotic modulus M_{os} is significantly smaller than the osmotic modulus K_{os} of the corresponding solution. This change is related to the presence of large-scale static nonuniformities in the gels, which are revealed by small-angle neutron scattering. A scattering function of the form $I(Q) = I_d(0)/(1 + Q^2\xi^2) + I_s(0)\exp\{-(Q\xi)^p\}$ is fitted to the neutron data, where Q is the transfer wave vector, ξ and Ξ are correlation lengths, and $p = 0.7$. Evaluation of $I_d(0)$ and $I_s(0)$, the intensities of the scattering due to dynamic and static concentration fluctuations, respectively, provides an independent estimate of M_{os} that is in satisfactory agreement with the value obtained by dynamic light scattering.

Introduction

Recently, progress has been made in the understanding of the relationship between the structural and the thermodynamic properties of swollen network systems.[1-5] By combining scattering observations of different length scales and macroscopic elastic and osmotic measurements, it has been found that a certain part of the network polymer is restrained from participating in the dynamic concentration fluctuations that govern the thermodynamics of the system.

One of the most important factors controlling the thermodynamic fluctuations in polymer solutions and gels is the quality of the solvent, which determines the statistics of the chain configurations. In good solvent conditions, the repulsive forces between polymer segments ensure excluded volume statistics, while in the Θ condition the chains adopt Gaussian statistics at all length scales owing to compensation between attractive and repulsive interactions.[6,7]

The scattering properties of polymer solutions are determined by the dynamic concentration fluctuations, which are simply related to the osmotic modulus. Long range uniformity is ensured by the osmotic pressure. In the absence of supermolecular ordering, polymer solutions usually exhibit a single correlation length,[7] ξ. In contrast, gels in general display an additional static scattering component. The excess scattering, caused by local nonuniformities in polymer concentration, depends on the distribution of cross-links in the system.

This paper deals with the scattering and osmotic properties of chemically cross-linked poly(vinyl acetate) (PVAc) gels swollen in different solvents. Measurements were made on gels in two good solvents, isopropyl alcohol (IPA) at 70 °C and acetone at 25 °C, and in a Θ solvent, IPA at 52 °C.

The osmotic moduli evaluated from quasi-elastic light scattering measurements are compared with those calculated from macroscopic osmotic observations. Comparisons are made between the gels and the corresponding solutions of the un-cross-linked polymer. In addition, data from small-angle neutron scattering provide an independent estimate of the longitudinal osmotic modulus M_{os}.

Theoretical Background

Scattering. The intensity of radiation scattered elastically from a polymer solution of polymer volume fraction φ is inversely proportional to the osmotic compressional modulus,[7] K_{os}

$$I(Q) = a\frac{kT(\rho_p - \rho_s)^2\varphi^2}{K_{os}}f(Q) \tag{1}$$

where a is a constant, $K_{os} = \varphi(\partial\Pi/\partial\varphi)$, Π being the osmotic pressure, ξ is the polymer-polymer correlation length, and $(\rho_p - \rho_s)^2$ is a contrast factor. The function $f(Q)$ describes the variation of the intensity with transfer wave vector $Q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the medium, λ is the incident wavelength, and θ is the scattering angle. In neutral polymer solutions in the range $Q\xi \leq 1$ the scattering form factor $f(Q)$ usually obeys an Ornstein-Zernike relation,[8]

$$f(Q) = (1 + Q^2\xi^2)^{-1} \tag{2}$$

In gels, the scattered intensity is governed by the longitudinal osmotic modulus[9]

$$M_{os} = K_{os|gel} + (4/3)G \tag{3}$$

where $K_{os|gel} = \varphi\partial\omega/\partial\varphi$, ω being the swelling pressure, and G is the shear modulus.

For light scattering experiments in polymer solutions, the scattering from concentration fluctuations is usually expressed in terms of the Rayleigh ratios,[10] $R(\theta)$

$$R(\theta) = R(\theta)_{solution} - R(\theta)_{solvent} = RTK\varphi/(\partial\Pi/\partial\varphi) \tag{4}$$

where K $(=16\pi^2n^2(\partial n/\partial c)^2/\lambda^4N_A)$ is an optical constant,

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[†] Universität Freiburg.
[‡] Eötvös Loránd University.
[§] Université Joseph Fourier de Grenoble.
[∥] CNRS associate laboratory.

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$\partial n/\partial c$ is the refractive index increment of the polymer-solvent system, λ is the wavelength of the radiation, and N_A is Avogadro's number.

The scattering function for a gel is the combination of two components:[1-4] the solution-like (dynamic) concentration fluctuations are described by eqs 1 and 2, while the static component of the scattering spectrum can take the form

$$I_s(Q) = I_s(0) \exp\{-(Q\xi)^p\} \qquad (5)$$

where Ξ is the mean radius of the static concentration fluctuations. The exponent p depends on the network structure.

Because of the presence of static scattering sources in gels, the significant thermodynamic parameters cannot be deduced from the total static light scattering intensity in a straightforward manner. By combining static and dynamic light scattering, however, the dynamic concentration fluctuations can be separated.[11] The static scatterers provide a local oscillator which heterodyne the light scattered by the fluctuating part of the system. The resulting heterodyned intensity correlation function is given by[12]

$$G(Q,\tau) = 1 + \beta[2X(1-X)g(Q,\tau) + X^2 g(Q,\tau)^2] \qquad (6)$$

where τ is the delay time, $g(Q,\tau)$ is the normalized field correlation function, and β is the coherence factor ($\beta \leq 1$). Here, $X = \langle I_F(Q)\rangle_T / \langle I(Q)\rangle_T$, where $\langle I_F(Q)\rangle_T$ is the time-averaged intensity of the fluctuating component and $\langle I(Q)\rangle_T$ is the total scattered intensity.

At the zero-time limit, eq 6 yields

$$X = 1 - \sqrt{1 + \beta - G(Q,0)}/\sqrt{\beta} \qquad (7)$$

where $G(Q,0)$ is the initial amplitude (at $\tau = 0$) of the intensity-intensity correlation function.

Thermodynamics. In the framework of the Flory-Huggins theory,[6] the osmotic pressure of a polymer solution can be expressed as

$$\Pi = -(RT/v)[\ln(1-\varphi) + (1 - P^{-1})\varphi + \chi\varphi^2 + w\varphi^3] \quad (8)$$

where v is the molar volume of the solvent, χ and w are the second- and third-order interaction parameters, and P is the degree of polymerization.

In swollen networks, the osmotic pressure of the network chains is assumed to have the same form as eq 8. In addition, however, an elastic pressure arises from the deformation of the chains and acts in opposition to the osmotic pressure.[13] The difference between these two terms yields the swelling pressure of the gel,

$$\omega = \Pi - G \qquad (9)$$

Experimental Details

Gel Preparation. PVAc gels were prepared by acetylation of cross-linked poly(vinyl alcohol) samples by a method described elsewhere.[14] The cross-linker was glutaraldehyde. For the experiments a fractionated PVA sample was used (M_w = 110 000). Cross-links were introduced at polymer concentrations c (3.0, 4.0, 5.0, 6.0, 7.0, and 8.0% w/w), and the molar ratio of monomer units to the molecules of cross-linker was 200 at each concentration. These samples are designated in the text by the two relevant numbers, e.g. 8/200, the first number referring to the initial polymer concentration and the second to the nominal chain length between cross-links.

For the calculation of the polymer volume fractions, φ, the density of pure PVAc (ρ_{PVAc} = 1.17 g cm^{-3}) was used.

Osmotic and Mechanical Measurements. The swelling pressure of the gels was measured as a function of the polymer concentration using a modified deswelling method.[15] Gels were brought to equilibrium with polymer solutions of known osmotic pressure. A semipermeable membrane was inserted between the gel and the solution to prevent the diffusion of the polymer molecules into the swollen network.

The shear modulus measurements were performed on isometric cylindrical gel specimens prepared in a special mould.[14] Swollen networks were uniaxially compressed (at constant volume) between two parallel flat plates. The stress-strain data were determined in the range of deformation ratio $0.7 < \Lambda < 1$. The absence of volume change and barrel distortion was checked by determining the dimensions of the deformed and undeformed gel cylinders.

Light Scattering Measurements. The light scattering experiments were performed in the angle range 30-150° using an ALV/SP-86 automatic goniometer (ALV, Langen, Germany) at 25 °C, with a Spectra Physics 2020 Krypton ion laser working at a wavelength of λ = 647.1 nm at approximately 300 mW. Intensity correlation functions were measured by an ALV-3000 multibit correlator (ALV, Langen, FRG). The analysis of the measured autocorrelation function was performed by inverse Laplace transformation using the program CONTIN,[16] as well as by cumulant analysis.[17]

The solution and gel samples were prepared in quartz test tubes of 8-mm inner diameter. Dust was removed from the solutions by filtering through 0.45-μm-pore Teflon filters. Calibration of the absolute intensity was obtained by using pure toluene.

In the dynamic measurements the intensity correlation function and the static scattered intensity were determined simultaneously at fixed positions of the sample. For the experimental setup the coherence factor, β, determined from measurements on a dilute suspension of polystyrene latex beads, was found to be 0.93 ± 0.02.

Small-Angle Neutron Scattering Measurements. The SANS measurements were performed on the D11 instrument at the Institut Laue-Langevin, Grenoble,[18] using an incident wavelength of 6 Å. The detector was placed at 4 and 16.5 m from the sample. The Q range explored was $0.003\ \text{Å}^{-1} \leq Q \leq 0.25\ \text{Å}^{-1}$, and counting times of between 20 min and 1 h were used. The ambient temperature during the experiments was 70 ± 1 °C.

The solvent was deuterated isopropyl alcohol (Janssen Chimica). The sample was placed between two 1-mm-thick quartz windows separated by a 1.8-mm-thick Viton O-ring. Corrections for incoherent background, detector response, and cell window scattering were made. Calibration of the scattered neutron intensity was performed using the signal from a 1-mm-thick water sample in conjunction with the absolute intensity measurements of Ragnetti et al.[19]

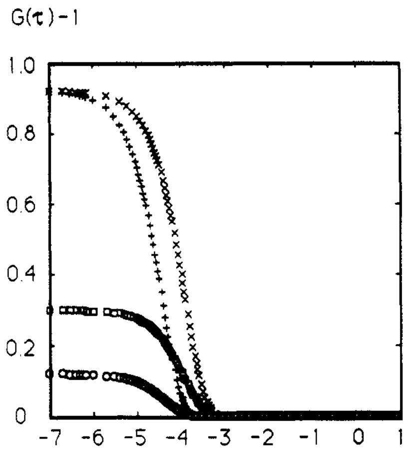

Figure 1. Intensity correlation functions at scattering angle Θ = 90° for a PVAc gel (○) and solution (+) at polymer volume fraction φ = 0.076 in isopropyl alcohol in good solvent conditions and at the Θ condition (×, solution; □, gel).

Results and Discussion

In Figure 1 typical intensity correlation functions are

Table I. Characteristic Relaxation Rates of the Field Correlation Functions from Dynamic Light Scattering in PVAc Gels and Solutions in Isopropyl Alcohol

sample	φ	$10^{-7}\Gamma/Q^2$(gel), cm^2 s^{-1}	$10^{-7}\Gamma/Q^2$(solution), cm^2 s^{-1}
		Good Solvent Condition	
1	0.076	6.0	3.9
2	0.101	7.3	4.9
3	0.127	8.7	5.8
4	0.152	9.8	6.6
5	0.177	10.7	7.4
6	0.203	12.5	8.2
		Θ Condition	
1	0.076	2.2	1.2
2	0.101	3.0	1.8
3	0.127	3.6	2.2
4	0.152	4.5	2.4
5	0.177	4.6	2.7
6	0.203	5.6	3.1

shown for a PVAc gel swollen in isopropyl alcohol at two different temperatures at volume fraction $\varphi = 0.076$ and the corresponding solutions. The correlation functions in both the solutions and the gels exhibit a single relaxation mode. In the gel the initial amplitude of the correlation function is significantly reduced, due to the presence of static light scattering from nonuniformities in the matrix. The characteristic relaxation time at the Θ condition is significantly longer than in the good solvent state.

From eq 6 it can be shown that

$$\mathrm{d}\{\ln[G(Q,\tau) - 1]\}/\mathrm{d}\tau|_{\tau=0} = -2\Gamma/(2 - X) \qquad (10)$$

where $\Gamma = -\mathrm{d}\ln[g(\tau)]/\mathrm{d}\tau|_{\tau=0}$ is the first cumulant of the field correlation function.

Table I lists the values obtained for the quantity[20] Γ/Q^2 for PVAc/isopropyl alcohol gels and solutions in good and Θ solvent conditions. In each case Γ/Q^2 for the gels systematically exceeds that of the solutions. Also, in good solvent conditions Γ/Q^2 is greater than at the Θ temperature. These findings are in agreement with the work of Brown et al.,[21] who recently investigated the relaxation behavior of PVAc solutions and gels, prepared using a procedure developed by us.[14] They obtained a single relaxation behavior both with acetone at 25 °C and with a Θ solvent (methanol at 6 °C) in solutions and in gels. Our own measurements qualitatively support their conclusions regarding the characteristic relaxation rates. In this paper we focus mainly on another objective: the thermodynamic information obtained from osmotic and scattering measurements.

The intensity of the fluctuating component of the scattered light (from eq 6 or 7), when combined with eq 4, yields the osmotic compressional modulus K_{os} of the solution or the longitudinal osmotic modulus M_{os} of the gel, respectively. In Figure 2 the values of K_{os} and M_{os} are shown for the PVAc/isopropyl alcohol system at 70 °C. It can be seen that at identical polymer concentrations the value of K_{os} is approximately twice that of M_{os}.

This finding is remarkable. Equation 3 suggests that, owing to the finite elasticity of the gel, the longitudinal osmotic modulus should be larger than the compressional modulus. The opposite is found. Moreover, on the basis of the relationship[9] $\Gamma/Q^2 = M_{os}/f$, where f is the polymer solvent friction coefficient, it is frequently assumed that the increase of Γ/Q^2 in the gel compared with that of a solution is the result of an increase in the osmotic modulus. This is not the case for the present gels.

The observed difference between K_{os} and M_{os} can result from at least two main effects: (i) modification of the thermodynamics of the system[22-24] and (ii) structural rearrangements in the polymer segments caused by cross-linking (a nonuniform concentration distribution modifies the average osmotic compressibility).[25] We start by comparing the macroscopic osmotic properties of the gels with those of the solutions.

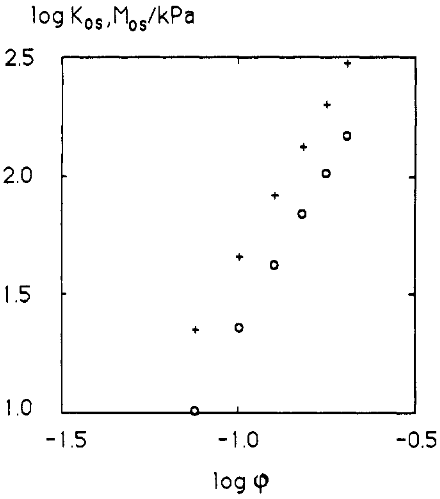

Figure 2. Comparison between K_{os} of PVAc/isopropyl alcohol solutions (+) and M_{os} of the gels (○) at 70 °C (good solvent conditions). Moduli were obtained from light scattering measurements.

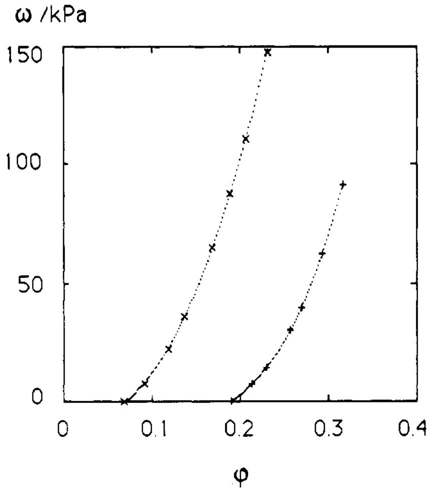

Figure 3. Variation of the swelling pressure ω with polymer volume fraction φ of a given PVAc gel sample (8/200) swollen in acetone (×) at 25 °C (good solvent condition) and in isopropyl alcohol gel (+) at 52 °C (Θ condition). The curves shown are the least squares fits of eq 11 through the data points.

In Figure 3 the dependence of the swelling pressure on the polymer volume fraction φ is shown for the same PVAc gel in two different solvents. The continuous curves through the experimental points are the least squares fits to the equation[13]

$$\omega = -(RT/v)[\ln(1-\varphi) + \varphi + \chi\varphi^2 + w\varphi^3] - G_0\varphi^{1/3} \qquad (11)$$

where R is the gas constant, v is the molar volume for the solvent, χ and w are interaction parameters, and G_0 is the elastic modulus of the gel in the unswollen state. The values found for these parameters are as follows:

PVAc/acetone at 25 °C

$$\chi = 0.416; \quad w = 0.362; \quad G_0 = 33.9\ \mathrm{kPa}$$

PVAc/isopropyl alcohol at 52 °C

$$\chi = 0.490; \quad w = 0.366; \quad G_0 = 29.7\ \mathrm{kPa}$$

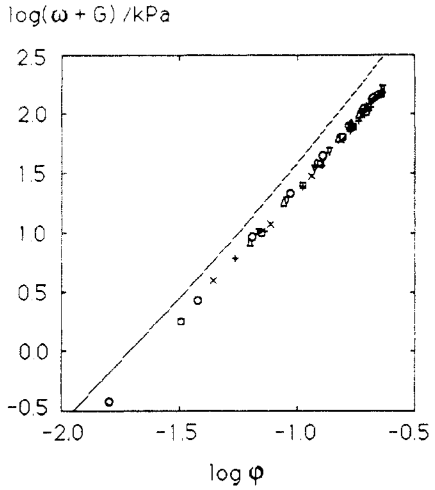

Figure 4. Mixing pressure $\omega + G$ as a function of polymer volume fraction φ for PVAc/acetone gels at 25 °C. The continuous line refers to the osmotic pressure of the solution of the un-cross-linked polymer at infinite molecular weight, using the data given in ref 27. Symbols: (○) 3/200; (□) 4/200; (×) 5/200; (+) 6/200; (△) 7/200; (▽) 8/200.

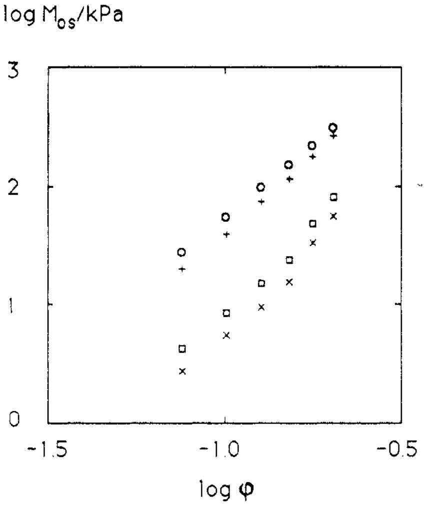

Figure 5. Longitudinal osmotic modulus M_{os} of PVAc gels in two different solvents at different concentrations, measured by light scattering and from the swelling pressure data. Gels in acetone at 25 °C: (+) light scattering; (○) swelling pressure. Gels in isopropyl alcohol at 52 °C: (×) light scattering; (□) swelling pressure.

Mechanical measurements of the elastic modulus of the same gel yielded G_0 = 31.6 kPa. The above values for χ and w in the case of isopropyl alcohol are consistent with these gels being in the Θ condition in the concentration range explored, according to the scheme of Daoud and Jannink.[26]

Equation 11 allows an estimate of the osmotic pressure Π (=$\omega + G$) of the cross-linked polymer to be made. In Figure 4 the values of $\omega + G$ for the PVAc/acetone system are shown as a function of the polymer volume fraction φ, for the gels as well as for the corresponding polymer solutions of infinite molecular weight, calculated using the data published by Vink.[27] The difference between the solution and gel curves indicates that the interaction parameters (χ and w) are significantly increased by the cross-links. The gel thus behaves as if a certain fraction of the swollen network were excluded from participating in the concentration fluctuations that control the osmotic pressure.

In Figure 5 the longitudinal osmotic moduli M_{os}, calculated from the fit of eq 11 to the macroscopic data, are compared with those measured by dynamic light scattering for PVAc/acetone at 25 °C and PVAc/isopropyl alcohol at 52 °C. It is apparent that M_{os} for the gels in the Θ solvent is significantly smaller than that for the same gels in the good solvent. The macroscopic values of M_{os} are in both cases close to those found by light scattering; i.e. the shortfall of M_{os} in the gel with respect to K_{os} in the solution (Figure 2) is consistent with the results of the independent thermodynamic observations. The residual systematic difference between the macroscopic and microscopic values for M_{os}, visible in Figure 5, is expected in systems exhibiting a nonuniform concentration distribution.[25]

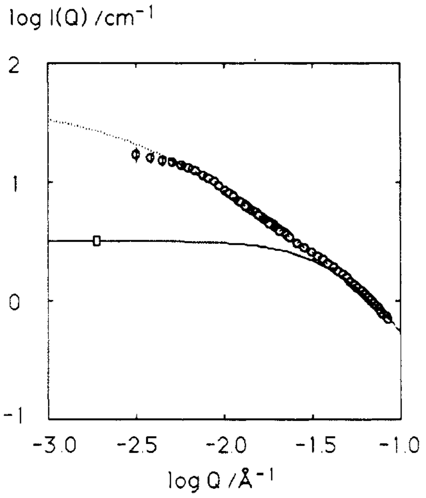

Figure 6. Neutron scattering intensity $I(Q)$, for the poly(vinyl acetate) gel 6/200 at φ = 0.152 in isopropyl alcohol at 70 °C. The dotted line is the least squares fit of the data to eq 12; the continuous line is the first term of eq 12 ($I_d(Q)$). The scattered light intensity from the concentration fluctuations, also shown (□), is plotted in the same units.

In order to obtain information on the concentration distribution of the nonuniformities, small-angle neutron scattering measurements were performed. In Figure 6 a neutron scattering spectrum is displayed for a PVAc/isopropyl alcohol gel at 70 °C. A quantitative estimate of the static nonuniformities can be obtained for this sample by fitting the experimental data to[3]

$$I(Q) = I_d(0)(1 + Q^2\xi^2)^{-1} + I_s(0)\exp\{-(Q\xi)^p\} \qquad (12)$$

where $I(Q)$, the total scattering intensity, is the sum of the dynamic (eq 1) and the static (eq 5) components. The dotted line in the figure is the least squares fit to the spectrum, where the value of p is taken to be 0.7, as reported previously.[3] (The parameters of this fit are $I_d(0)$ = 3.13 cm^{-1}, $I_s(0)$ = 47.1 cm^{-1}, ξ = 23.9 Å, Ξ = 307 Å.) The continuous line is the Ornstein–Zernike function obtained from this decomposition procedure. The square represents the intensity obtained from dynamic light scattering measurement, when expressed in the same units. The agreement between the values found for the intensity of the dynamic component is satisfactory.

Conclusions

The osmotic properties of chemically cross-linked PVAc gels swollen in different solvents have been investigated by osmotic and scattering techniques. In these lightly cross-linked gels the longitudinal osmotic modulus M_{os} is found to be approximately half the value of the osmotic modulus K_{os} of the corresponding solution. The relaxation rates of the concentration fluctuations, measured by dynamic light scattering, are, however, greater in the gels than in the corresponding solutions. It is shown that the macroscopic measurements of M_{os} are consistent with those found from light scattering.

Small-angle neutron scattering measurements indicate the presence of static nonuniformities in the gels having a wide size range. When a scattering function was fitted to the data consisting of a stretched exponential for the static part of the spectrum and an Ornstein–Zernike relation for the dynamic part, an estimate of M_{os} was made, which is in satisfactory agreement with the value obtained by dynamic light scattering.

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