Decisive test of the ideal behavior of tetra-PEG gels

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The objective of this work is to investigate the thermodynamic and scattering behavior of tetra-poly(ethylene glycol) (PEG) gels. Complementary measurements, including osmotic swelling pressure, elastic modulus, and small angle neutron scattering (SANS), are reported for a series of tetra-PEG gels made from different molecular weight precursor chains at different concentrations. Analysis of the osmotic swelling pressure *vs* polymer volume fraction curves makes it possible to separate the elastic and mixing contributions of the network free energy. It is shown that in tetra-PEG gels these free energy components are additive. The elastic term varies with the one-third power of the polymer volume fraction and its numerical value is equal to the shear modulus obtained from independent mechanical measurements. The mixing pressure of the cross-linked polymer is slightly smaller than that of the corresponding solution of the uncross-linked polymer of infinite molecular weight but it exhibits similar dependence on the polymer concentration. The observed deviation between the osmotic mixing pressures of the gel and the solution can be attributed to the presence of small amount of structural inhomogeneities frozen-in by the cross-links. SANS reveals that the scattering response of tetra-PEG gel is mainly governed by the thermodynamic concentration fluctuations of the network, i.e., the contribution from static inhomogeneities to the SANS signal is small. [<http://dx.doi.org/10.1063/1.4982253>]

INTRODUCTION

Understanding of the physics of polymer gels and testing the validity of different theoretical models requires making an array of high quality measurements on “ideal” networks. However, the requirement of ideality cannot be easily met, partially because polymer networks always contain structural inhomogeneities. Cross-linking generates defects in the network structure such as pending chains, loops, entanglements, unreacted functionalities, and spatial nonuniformities in the distribution of the polymer and/or cross-links. In other words, the topology of real networks usually deviates from the ideal networks.^{1–15} The latter is defined as a homogeneous collection of ideal (Gaussian) chains connecting neighboring cross-links in which all functionalities are attached to the ends of the polymer chains.

Chemically cross-linked (covalent) networks are typically formed in three different ways:

- cross-linking of existing linear polymer chains,
- polymerization of reactive monomers or prepolymers, and
- copolymerization of existing chains.

Network formation is a statistical process, i.e., cross-links are introduced in a random manner and, therefore, the resulting systems do not have a well-defined topology. The type of defects strongly depends on how the network has been made.

Due to the finite molecular weight of the polymer, pendant chains are always present in networks formed by cross-linking of existing chains either in solution or in the melt (vulcanization). The number of pendant chains (dangling ends) is inversely proportional to the molecular weight of the polymer. Networks cross-linked by radiation (e.g., UV or high energy electron beam) contain many pendant chains, which may also arise from chain-scission occurring in the course of the cross-linking process. Cross-linking in solution usually results fewer trapped entanglements compared to cross-linking in the melt, but loop formation may become pronounced. Complete monomer conversion in the polymerization and cross-linking process is very unlikely. There is always residual polymer (oligomers, short chains, cyclic structures, etc.), which is not attached to the network. In the case of radical polymerization (e.g., peroxide and persulfate curing), radical fragments may chemically contaminate the polymer chains.

In general, by using prepolymers the topology of the resulting network is better controlled. For example, end-linking of bifunctionally terminated chains with a multifunctional cross-linker results networks in which the length of the network chains is defined by the molecular weight of the prepolymer, and the functionality of the cross-links is equal to that of the cross-linker. In an ideal end-linked polymer network, all chains are connected at both ends to the junctions (cross-links) and all cross-links are connected to the network. End-linked model networks were made from a variety of polymers, e.g., from poly(dimethylsiloxane) (PDMS), and aimed to gain more insight into the relationships between the molecular architecture and physical properties (elastic

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modulus, stress-strain relationship, etc.). However, these systems also contain defects, e.g., pendant chains, loops, and unreacted functionalities.

In cross-linked systems, the nominal molecular weight of the polymer is infinite and the elastic response is defined by the equilibrium modulus, which is proportional to the cross-link density. Network defects discussed above may significantly affect the macroscopic mechanical and swelling properties of the gels. Unlike in ideal elastic solids, in gels the polymer chains can rearrange and dissipate energy. Because in the gel the ends of the cross-linked chains are attached to the junctions, the network chains relax more slowly than the free (uncross-linked) chains in solution. The relaxation of pendant chains is also slower than that of the free chains because one of their ends is attached to the network.

In a set of recent papers, Shibayama and co-workers reported that tetra-poly(ethylene glycol) (PEG) gels exhibit a near-ideal polymer network topology.^{16–25} These gels were made by A-B type cross-end coupling of two tetra-arm poly(ethylene glycol) (PEG) units that had mutually reactive amine (TAPEG) and activated ester (TCPEG) terminal groups (tetra-PEG units). The tetra-PEG gels exhibit both high deformability (~900%) and high breaking strength (~30 MPa).

Based on systematic studies made on swollen tetra-PEG networks, the authors demonstrated that

- (1) these systems contain only a small number of pendant chains, trapped entanglements, and elastically ineffective loops,¹⁹ and
- (2) the elasticity of tetra-PEG gels is well described by the phantom network model.²¹

The authors also made small angle neutron scattering (SANS) measurements on these gels and found that the shape of the SANS profiles (i) resembled that of polymer solutions and (ii) could be described by an Ornstein-Zernike form factor. These findings were interpreted as evidence for the absence of network nonuniformities.

Clearly, the extremely careful studies of Shibayama *et al.* on tetra-PEG gels represent the most comprehensive investigation made on near-ideal polymer gels and provide tremendous insight into the mechanical and scattering behavior of the tetra-PEG system. However, previous studies have not addressed directly the thermodynamics of these gels. Swelling and osmotic properties are critically important to probe the assumptions of existing network models such as the separability and additivity of the free energy components. In addition, osmotic swelling pressure measurements provide an independent estimate of the intensity arising from the thermodynamic concentration fluctuations in the SANS response.^{26–34}

In the present work we report systematic osmotic swelling pressure and elastic (shear) modulus measurements made on several sets of tetra-PEG gels. We vary the cross-link density of the gels and the polymer concentration at which the cross-links are introduced. Two basic assumptions of the Flory-Rehner theory are tested (i) the additivity/separability of the osmotic and mixing contributions to the osmotic swelling pressure and (ii) the effect of cross-links on the mixing pressure of the network polymer. Furthermore, we compare the

total SANS intensity with the intensity estimated independently from macroscopic osmotic swelling pressure and shear modulus measurements.

The paper is organized as follows. First we describe the osmotic properties of tetra-PEG gels and analyze the osmotic swelling pressure curves in the framework of the Flory-Rehner model. We determine the mixing pressure of the cross-linked polymer from osmotic swelling pressure and shear modulus measurements. Then the structure of the gels at smaller length scales is investigated by SANS. The SANS profile of the gel is compared with that of the corresponding solution of the uncross-linked polymer. The thermodynamic component of the SANS response is independently estimated from the longitudinal osmotic modulus determined from macroscopic measurements. A comparison is made between the SANS and osmotic results in gels made at different initial polymer concentrations with different cross-link densities.

THEORETICAL BACKGROUND

Osmotic properties

The Flory-Rehner theory^{35–37} of network swelling assumes additivity between the free energy of mixing of the polymer chains and the solvent molecules (ΔF_{mix}) and the free energy of the deformation of the network chains (ΔF_{el}),

$$\Delta F = \Delta F_{\text{mix}} + \Delta F_{\text{el}}. \quad (1)$$

In a gel, the relevant osmotic property is the osmotic swelling pressure Π_{sw} , i.e., the excess pressure required to maintain the gel at constant composition when it is equilibrated with a solvent or a solution. Π_{sw} is the sum of the osmotic mixing pressure Π_{mix} and the elastic pressure Π_{el} . The former tends to expand the gel, while the latter causes shrinking,

$$\Pi_{\text{sw}} = - \frac{1}{V_1} \frac{\partial \Delta F}{\partial n_1} = \Pi_{\text{mix}} + \Pi_{\text{el}}, \quad (2)$$

where V_1 is the partial molar volume of the solvent and n_1 is the number of moles of the solvent.

Π_{mix} can be described by a Flory-Huggins type expression^{38,39}

$$\Pi_{\text{mix}} = -(RT/V_1)[\ln(1 - \varphi) + \varphi + \chi_0\varphi^2 + \chi_1\varphi^3], \quad (3)$$

where φ is the volume fraction of the polymer, χ_0 and χ_1 are interaction parameters, R is the gas constant, and T is the absolute temperature.

In gels, $\Pi_{\text{el}} = -G$, where the numerical value of G is equal to the shear modulus. In ideal networks according to the theory of rubber elasticity^{36,37} G varies with the polymer volume fraction as

$$G = G_0\varphi^{1/3}, \quad (4)$$

where G_0 is a constant. $G_0 = ARTv/V_0$, where v is the moles of the elastic chains in the network and V_0 is the volume of the unswollen (dry) network.

It was found experimentally that Π_{mix} is smaller in the gel than in the corresponding uncross-linked polymer solution.⁴⁰ This reduction may be attributed either to changes in the polymer-solvent interaction parameter or to changes in the distribution of the polymer due to cross-linking.

Scattering behavior

Small-angle neutron scattering (SANS) is a powerful method to investigate the structure of polymers over a broad range of length scales, $10 \text{ \AA} < q^{-1} < 500 \text{ \AA}$, where q is the scattering wave vector, $q = [(4\pi/\lambda)\sin(\theta/2)]$, θ is the scattering angle, and λ is the wavelength of the incident radiation. Scattering measurements yield information on the spatial distribution of the polymer segments. Multicomponent polymer systems, such as polymer solutions and gels, display fluctuations in component concentration that lead to small-angle scattering. In an ideal polymer solution of overlapping polymer chains, the scattering intensity arising from thermodynamic concentration fluctuations is given by^{26,41}

$$I_{\text{SOL}}(q) = a \frac{KT(\rho_p - \rho_s)^2 \varphi^2}{K_{\text{OS}}} \frac{1}{1 + (q\xi)^2}, \quad (5)$$

where ρ_p and ρ_s are the scattering length densities of the polymer and solvent, respectively, $K_{\text{OS}} [= \varphi(\partial\Pi_{\text{mix}}/\partial\varphi)]$ is the osmotic compression modulus of the solution, ξ is the polymer-polymer correlation length, a is a constant (of order unity), and kT is the Boltzmann factor.

In polymer gels, the scattering intensity from the thermodynamic fluctuations is governed by the longitudinal osmotic modulus $M_{\text{OS}} [= \varphi(\partial\Pi_{\text{sw}}/\partial\varphi) + 4G/3]$, which replaces K_{OS} in Equation (5). Furthermore, gels generally contain static inhomogeneities, which contribute to the overall scattering response. The static scattering component $I_{\text{STATIC}}(q)$ is intrinsically different from the first (thermodynamic) component and should be treated differently.

The total scattering intensity from a neutral gel is described by the sum of two contributions,

$$I_{\text{GEL}}(q) = I_{\text{DYNAMIC}}(q) + I_{\text{STATIC}}(q) \\ = a \frac{kT(\rho_p - \rho_s)^2 \varphi^2}{M_{\text{OS}}} \frac{1}{1 + (q\xi)^2} + I_{\text{STATIC}}(q), \quad (6)$$

where the functional form of the first term is similar to that of the polymer solution (see Eq. (5)) and the second term is due to inhomogeneities frozen in by the cross-links. The form factor of the second term depends on the preparation conditions of the gels (cross-linking polymerization, photopolymerization, end-linking, vulcanization, etc.).^{42–44} In an ideal (defect-free) network the second term is negligible.

MATERIALS AND METHODS

Gel preparation

Tetra-PEG gels were made by a procedure described elsewhere.^{17,45} Tetra-amine-terminated PEG and tetra-NHS-glutarate-terminated PEG (TNPEG) were prepared from tetrahydroxyl-terminated PEG (THPEG) having equal arm lengths. Here NHS represents N-hydroxysuccinimide. The molecular weights (M_w) of TAPEG and TNPEG were matched. Three sets of samples having different M_w values (10, 20, and 40 kDa) were made. Gels were prepared at six polymer concentrations (20, 40, 60, 80, 100, and 120 mg/ml) from each polymer. The sample code is defined by M_w and the polymer concentration of cross-linking. For example, 10/20 is

a tetra-PEG gel made from $M_w = 10$ kDa precursor chains at 20 mg/ml concentration.

Tetra-PEG gels were synthesized as follows. Equal amounts of TAPEG and TNPEG (20–120 mg/ml) were dissolved in phosphate buffer (pH = 7.4) and phosphate-citric acid buffer (pH = 5.8), respectively. The buffer solutions were made with D_2O . The reaction rate was controlled by choosing the following ionic strengths for the buffers: 25 mM for lower macromer concentrations (20–100 mg/ml) and 75 mM for high concentration (120 mg/ml) for tetra-PEG-10. For tetra-PEG 20 and tetra-PEG 40 the ionic strengths of the buffers were 50 mM for lower macromer concentrations (20–100 mg/ml) and 100 mM for the highest macromer concentration (120 mg/ml). The two solutions were mixed, and the resulting mixture was poured into a mold. The completion of the cross-linking reaction required approximately 12 h.

Small-angle neutron scattering (SANS) measurements

SANS measurements were made on the 2D SANS instrument, SANS-U of the University of Tokyo, located in the JRR-3 Research Reactor, Japan Atomic Energy Agency, Tokai, Ibaraki, Japan. A monochromated cold neutron beam with an average neutron wavelength of $7.00 \text{ \AA}$ and 10% wavelength distribution was used. The scattered neutrons were counted with a 2D-detector (Ordela 2660N, Oak Ridge). The sample-to-detector distances were chosen to be 2 and 8 m for the measurements. After corrections for open beam scattering, transmission, and detector inhomogeneities, the corrected scattering intensity functions were normalized to the absolute intensity scale with a polyethylene secondary standard. Incoherent scattering subtraction was made using the method of Shibayama *et al.*^{46,47}

Osmotic swelling pressure measurements

Osmotic swelling pressure measurements were made by equilibrating the gels enclosed in a semipermeable membrane by aqueous solutions of poly(vinylpyrrolidone) (PVP, 29 kDa) of known osmotic pressure.^{48–50} At equilibrium, the osmotic swelling pressure of the gel inside the dialysis bag is equal to the osmotic pressure exerted by the polymer solution outside. When equilibrium was reached, gel samples were removed from the dialysis bags, weighed, and dried. The procedure results for each gel the dependence of Π_{sw} upon the polymer volume fraction, φ .

Elastic modulus measurements

The mechanical response of the tetra-PEG gels was determined from stretching measurements and also from uniaxial compression tests.

The stretching measurements were performed on dumbbell-shaped films using a mechanical testing apparatus (Rheometer: CR-500DX-SII, Sun Scientific, Co.) at a crosshead speed of 0.1 mm/s . The gel samples were used in the “as-prepared” state. Each specimen was stretched and released repeatedly two times, and the reproducibility of the results was confirmed. More than 10 samples were tested for each network concentration and the observed moduli were arithmetically averaged.

The shear moduli of the tetra-PEG gels were also determined from uniaxial compression measurements made by a TA.XT2I HR texture analyzer (Stable Micro Systems, U.K.). This apparatus measures the deformation as a function of the applied force. Cylindrical gel specimens were uniaxially compressed (at constant volume) between two parallel flat glass plates. Typical sample sizes were 2-3 mm in height and 10-30 mm in diameter. Measurements were made in the range of deformation ratios $0.8 < \Lambda < 1$ ($\Lambda = L/L_0$, L and L_0 being the lengths of the deformed and undeformed gel specimen, respectively). The elastic (shear) modulus, G_s , was calculated from the nominal stress, σ (force per unit undeformed cross section), using the following equation:^{36,37}

$$\sigma = G_s (\Lambda - \Lambda^{-2}). \quad (7)$$

Typical duration of a stress-strain measurement was between 5 and 10 min. No volume change was observed during the experiment. The agreement between the stretching and uniaxial compression measurements was within 10%. The osmotic swelling pressure and mechanical measurements were carried out at $25 \pm 0.1^\circ\text{C}$.

The reproducibility of the whole procedure, including gel preparation, osmotic swelling pressure, and modulus measurements, and SANS was found to be within 4%-5%.

RESULTS AND DISCUSSION

In this section we make multiple comparisons between theoretical predictions and experimental findings. First we analyze the osmotic swelling pressure data of tetra-PEG gels and

FIG. 1. Variation of the shear modulus G_s of tetra-PEG gels as a function of the polymer volume fraction ϕ for gels prepared from the 10 kDa prepolymer at different concentrations. The lines through the data points are least squares fits of Equation (8). Inset: dependence of A and m on the concentration of cross-linking.

separate the elastic and mixing components. The elastic term is compared with the elastic (shear) modulus determined by mechanical measurements and the mixing pressure is compared with the osmotic pressure of the solution of the uncross-linked polymer. Then the SANS profiles of tetra-PEG gels are

FIG. 2. Osmotic swelling pressure Π_{sw} vs polymer volume fraction ϕ plots for tetra-PEG gels made from 10 kDa (a), 20 kDa (b), and 40 kDa (c) precursor chains at different polymer concentrations. Designation of the samples: molecular weight of precursor chains (kDa)/polymer concentration at cross-linking (mg/ml). The continuous curves are least squares fits of Equation (9) to the experimental data. Inset: variation of the interaction parameters χ_0 and χ_1 as a function of the polymer concentration of cross-linking.

compared with the scattering response of the corresponding solutions. We also estimate the scattering profiles of the gels from osmotic swelling pressure measurements. A comparison is made between the longitudinal osmotic moduli obtained from SANS and those calculated from macroscopic osmotic swelling pressure and shear modulus measurements.

Elastic modulus of tetra-PEG gels

Figure 1 shows the dependence of the shear modulus as a function of the polymer volume fraction for tetra-PEG gels made from 10 kDa precursor chains at six different polymer concentrations.

The continuous lines through the data points are least squares fits of the following equation:

$$G_s(\varphi) = A\varphi^m, \quad (8)$$

where A and m are fitting parameters. The inset in Figure 1 shows the variation of A and m as a function of the polymer concentration at which the gels were made. The value of A is proportional to the cross-link density and m ($= 0.33 \pm 0.01$) is in good agreement with the prediction of the theory of rubber elasticity (see Eq. (4)).

Analysis of the osmotic swelling pressure measurements

Figure 2 shows the osmotic swelling pressure vs polymer volume fraction curves for all tetra-PEG gels.

The Π_{sw} vs φ plots were analyzed by fitting Equation (9) to the experimental data

$$\Pi_{sw} = -(RT/V_1)[\ln(1 - \varphi) + \varphi + \chi_0\varphi^2 + \chi_1\varphi^3] - B(\varphi/\varphi_e)^{1/3}, \quad (9)$$

where φ_e is the volume fraction of the polymer in the fully swollen gel and B is a constant. The inset in the figures shows

FIG. 3. $G [= B(\varphi/\varphi_e)^{1/3}]$ from osmotic swelling pressure measurements as a function of G_s from uniaxial compression tests made at the concentration of gel preparation. Symbols: 10 kDa (circles), 20 kDa (triangles), 40 kDa (squares). Continuous line through the data points is a guide to the eyes.

the variation of the interaction parameters (χ_0 and χ_1) for each set of data. It can be seen that χ_0 and χ_1 only weakly depend on the concentration at which the gels are made. However, the molecular weight of the precursor chains affects χ_1 . The observed decrease of χ_1 suggests that the thermodynamic quality of the solvent improves, which may be caused by the hydrophilic nature of the cross-linker.

In Figure 3 is plotted the second term of Equation (9) [$G = B(\varphi/\varphi_e)^{1/3}$] obtained from the fits as a function of G_s determined from uniaxial compression measurements made at the concentration of cross-linking. The agreement between the values obtained by the two entirely different and independent methods is good.

The present result implies that in these tetra-PEG gels (1) the elastic contribution is indeed separable from the total free energy and (2) the total free energy can be treated as the sum of an elastic and a mixing term. However, it does not follow from these results that the mixing term of the gel is identical with the mixing pressure of the corresponding uncross-linked polymer solution, which is one of the basic requirements for ideal polymer gels. In general, cross-linking may affect the polymer-solvent interaction parameter because the cross-linker modifies the chemical composition of the system and generates inhomogeneities in the gel.

To evaluate the effect of cross-linking on the osmotic mixing pressure of tetra-PEG gels we compared the sum $\Pi_{mix} = \Pi_{sw} + G_s$ determined from experimental data with the osmotic pressure of PEG solution Π_{sol} calculated by the following equation:

$$\Pi_{sol} = -(RT/V_1)[\ln(1 - \varphi) + (1 - P^{-1})\varphi + \chi_0\varphi^2], \quad (10)$$

where P is the degree of polymerization (for the cross-linked polymer $P = \infty$) and $\chi_0 = 0.426$.⁵¹

FIG. 4. Osmotic mixing pressure Π_{mix} ($= \Pi_{sw} + G_s$) for tetra-PEG gels and solutions. Different symbols refer to gels made at different polymer concentrations from 40 kDa precursor chains. The continuous curves through the data points are guides to the eyes. The upper curve is the osmotic pressure Π_{sol} for the solution of the uncross-linked PEG of infinite molecular weight calculated by Equation (10).

FIG. 5. SANS profiles of tetra-PEG gels and the corresponding uncross-linked solutions. The gels were made from the 20 kDa precursor chains. The dashed curves through the solution data points are guides to the eyes. For clarity each curve is multiplied by a factor of 10 with respect to the previous lower polymer concentration.

Figure 4 shows that all gel data fall on a master curve, i.e., no effect of cross-link density is detectable. Π_{mix} for the cross-linked polymer is slightly smaller than that for the solution of the uncross-linked polymer, but both data sets exhibit similar dependence on the polymer volume fraction. Reduction of the osmotic pressure observed in many other gel systems is the signature of network inhomogeneities.^{26,52–54} In the present system, however, the difference between the solution and gel data is much smaller than in the previously studied systems. Thus, we can conclude that the osmotic behavior of the present tetra-PEG gels is nearly ideal.

Comparison between the results of osmotic swelling pressure measurements and SANS observations

The ultimate test of network ideality is to compare the results of independent macroscopic and microscopic (scattering) observations made on the same gels. In the section titled

FIG. 7. A comparison between M_{os} deduced from the SANS profiles with M_{os} calculated from osmotic swelling pressure and shear modulus measurements. Symbols: 10 kDa (circles), 20 kDa (squares), 40 kDa (triangles).

Theoretical Background, we pointed out that the scattering intensity of an ideal polymer solution at the thermodynamic limit ($q \rightarrow 0$) is governed by the osmotic compression modulus, K_{os} . In gels, the corresponding quantity is the longitudinal osmotic modulus, M_{os} . Consequently, M_{os} can be determined from the intensity of the thermodynamic component of the SANS signal. The longitudinal modulus can also be estimated independently from osmotic swelling pressure and shear modulus measurements.

In an ideal gel the static scattering contribution to the SANS intensity should be negligible. To test the validity of this requirement in Figure 5 we compared the SANS profiles of tetra-PEG gels and solutions measured at the same concentrations. In the gels small excess scattering is detectable at the lowest values of q . However, in all other regions explored in the SANS experiment, the solution and gel data agree within the experimental uncertainties.

On the basis of the results shown in Figure 5, we can now compare the measured and calculated SANS profiles of tetra-PEG gels (Figure 6). The latter were estimated from the

FIG. 6. SANS profiles of gels made from 40 kDa precursor chains at three polymer concentrations (a) and from different molecular weight (10 kDa, 20 kDa, and 40 kDa) precursor chains at 100 mg/ml polymer concentration (b). The continuous curves are calculated from M_{os} and G_s together with the correlation lengths obtained from the fit of Equation (5) to the SANS data. For clarity each curve is multiplied by a factor of 10 with respect to the previous lower polymer concentration (a) or lower molecular weight of the precursor chains (b).

macroscopic longitudinal and shear moduli together with the correlation lengths obtained from the fits of Equation (5) to the SANS spectra (not shown here). It can be seen that the calculated curves (continuous curves) are in excellent agreement with the experimental data.

In Figure 7 are compared the longitudinal osmotic moduli of tetra-PEG gels from macroscopic measurements with those deduced from the SANS signal. The agreement between the values obtained by these completely independent techniques probing entirely different length scales is reasonable.

CONCLUSIONS

Systematic osmotic swelling pressure and elastic modulus measurements made on tetra-PEG gels bring evidence for the near ideal behavior of these gels. The osmotic swelling pressure can be separated into two components: a mixing pressure term describing the mixing of the network chains with the solvent molecules and an elastic term governing the elastic response of the swollen network. It is shown that

1. the elastic and mixing free energy contributions are separable and additive,
2. the elastic contribution derived from osmotic swelling pressure measurements is equal to the shear modulus of the swollen network, and
3. the mixing pressure of the network polymer is slightly smaller than that of the osmotic pressure of the solution of the corresponding uncross-linked polymer. In the latter case the deviation between the solution and gel data is small (less than 10%) indicating that the present gels contain only small amount of inhomogeneities.

It is also demonstrated that the shape of the SANS spectra of tetra-PEG gels and solutions is very similar. In gels at low values of q , excess scattering is observed indicating the presence of large static scatterers, the contribution of which to the thermodynamic concentration fluctuations is negligible. This finding is consistent with the reduced osmotic mixing pressure of the network polymer observed by osmotic pressure measurements. The osmotic moduli of tetra-PEG gels derived from SANS measurements are in reasonable agreement with those calculated from osmotic swelling pressure and elastic modulus measurements.

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