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Small Angle Neutron Scattering Study of End-Linked Gels

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ABSTRACT: Monomer concentration fluctuations in end-linked gels are investigated as a function of the swelling ratio with the help of small angle neutron scattering. The signals scattered by the gels are compared to those of semidilute solutions of linear chains of the same concentration. It is shown that the gels scatter a signal at small angles much stronger than the equivalent solutions. Such a scattering excess is attributed to the presence of two types of heterogeneities in the gel. Two different types of behavior are observed: at intermediate values of the scattering vector, q, the spectra exhibit a "shoulder" suggesting that "starlike" objects are present in the gel while at very small angles, the scattering intensity, $I(q)$, increases very strongly with q. In a log representation, the scattering intensity is roughly described by $\sim \phi q^{-3}$. This scattering law at small values of q is interpreted in terms of a distribution of starlike objects in space.

1. Introduction

The existence of large-scale polymer concentration fluctuations in polymer gels has been brought to attention with the help of solvent permeability experiments[1] and small angle scattering experiments.[2–4] In particular, a systematic study on statistical gels, using small angle neutron scattering (SANS), was carried out recently.[5] It was shown that statistical gels, synthesized from the random cross-linking of semidilute solutions of very long chains, exhibit a scattering excess with respect to the solutions (the solvent being labeled with respect to the polymer). This was interpreted in terms of heterogeneous structures. At the preparation concentration, the gel scatters the same signal as the semidilute solution of precursor chains. This means that, at least for the cross-linking volume fraction used ($\phi_x \sim 0.8\%$ in mole/mole of monomer unit), the cross-link points do not introduce new significant correlations with respect to the precursor solution. When the gel is swollen with respect to the preparation concentration, it scatters a stronger signal, at small angles, than a solution at the new concentration. The interpretation was that swelling the network causes a "screening breakdown" of the initial random distribution of cross-linking points in space at the preparation concentration. In other words, in a swollen state, concentration fluctuations in the gel are revealed. More precisely, a theoretical model based on a percolation of blobs was proposed.[6] In this model, the semidilute solution is mapped in a lattice of size ξ into which cross-linking points are introduced at random. ξ is the screening length of the semidilute solution, that is, the blob size. It is important to stress the fact that, since the chains are very long, each one is expected to contain a large number of independent blobs. Thus, the random cross-linking process gives rise to the formation of a terminated gel (well above the gel point of the chains in the vessel) even if the system is below the gel point of the blobs. After the random cross-linking process, below the blob gel point, clusters of frozen blobs (percolation animals) will be present in the system. Such zones, richer in cross-linking points than the average in the gel, are harder to deform than the interstitial "soft zones" which are poor in cross-link points. Such "hard zones" are grown in an interspersed manner in the reaction bath, that is, in a strongly screened situation. Since they are harder to deform than the soft zones of the gel, they are separated upon swelling (or stretching); that is, the screening is broken down. This spatial separation of the hard zones is responsible for the formation of concentration fluctuations at large scales. Consequently, according to this approach, an increase in scattering intensity at small angles should be observed, contrary to classical swelling theories,[7] which consider the mesh size of the network as the largest length scale at which correlations exist in the system. In the blob percolation model, the length scale associated with the homogeneity of the system is related to the mean screening distance between hard zones. From data, it was possible to obtain the variation of a screening length, ξ_{gel}, with polymer volume fraction ϕ. It was shown[5] that it follows a scaling law, the exponent of which, is stronger than that associated with the variation of the same quantity in semidilute solutions, $\xi_{\mathrm{sol}} \sim \phi^{-0.77}$. For the gel synthesized with a cross-link volume fraction $\phi_x = 0.8\%$, one finds $\xi_{\mathrm{gel}} \sim \phi^{-1.68}$, which is in good agreement with the predictions of the model briefly recalled above ($\xi_{\mathrm{theor}} \sim \phi^{-5/3}$).

The picture described above should not, however, apply to end-linked short chains gels. In this case, the size of the blob and the size of the precursor chain are of the same order of magnitude in the preparation concentration, and one cannot, in principle, map the cross-linking process into a percolation of blobs problem. The only available information is given by classical elasticity models,[8] and some extensions of them,[9] which implicitly assume homogeneity above the mesh length scale ("perfect network") and a recent calculation by Vilgis which considers the influence of small cross-linking fluctuations in the small angle scattering.[10] In this context, we decided to study end-linked gels from an experimental point of view, using the same experimental approach used for statistical gels, that is, to compare the scattering of gel and semidilute solutions of the same concentration, which are taken as "homogeneous" reference systems. The study presented in this paper was carried out on gels synthesized by end-linking small ($M_w \sim 22\,000$), and quite monodisperse ($M_w/M_n \sim 1.2$), chains. In the next section we present a brief recall of the synthesis employed. In section 3, results of the small angle neutron scattering study of these networks

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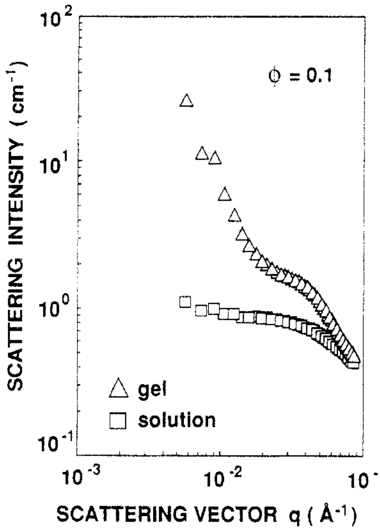

Figure 1. Scattering intensity as a function of the scattering vector amplitude q, for the end-linked gel and for a semidilute solution at a polymer volume fraction $\phi = 0.1$. This concentration is very close to the concentration of the gel at the preparation state. A log $(I(q)) \times \log(q)$ representation is used.

compared to semidilute solutions of the same concentration are presented. We end the article with some considerations about the structure of these swollen networks.

2. Experimental Section

The end-linked network was prepared by an anionic block copolymerization of styrene and the tetrafunctional divinylbenzene (DVB) molecule. The method is described in detail in ref 11. In such a synthesis, the initial step involves the growth of bifunctional polystyrene chains with living ends in a tetrahydrofuran (THF) toluene mixture at −70 °C. DVB molecules added to the solution are able either to polymerize between themselves or to react with the polymer living ends. As a result, a network is formed in which DVB "nodules" act as cross-links. The sample was synthesized with an average of three DVB molecules per "living" polymer end, and the average functionality, f, of these nodules has been estimated in the past to be about 5–6.[12] Therefore, there is no direct independent measure of f. GPC analysis of the precursor chains showed that the chains have a mean molecular weight of 22 000, with very low polydispersity. The volume fraction of polymer in the reaction bath was 0.098. The elastic modulus, measured by uniaxial compression of the gel swollen at equilibrium in toluene ($Q_{\max} \sim 23$) is $G = 2664$ Pa. The values of these two macroscopic physical quantities (G and $Q_{\max}$) are very close to the values obtained for the statistical gel of ref 5. After synthesis, the samples were washed in THF, dried, cut, and polished into disks. For each dried disk, an optimum size, previously calculated, was obtained and, upon swelling in commercial deuterated toluene, the samples fitted perfectly the neutron scattering quartz cell (15.0 mm × 1.0–3.0 mm).

Neutron scattering experiments were carried out at Institut Laue-Langevin (ILL) at Grenoble, using spectrometers D17 (sample detector distance $d = 2.75$ m and incident wavelength $\lambda = 6.9$ Å) and D11 ($d = 10.0$ m, $\lambda = 10.1$ Å). Standard procedures of data treatment were employed: the detector normalization was obtained using the flat incoherent scattering of water at the same experimental conditions, and the absolute coherent scattering intensity was obtained by subtracting the appropriate incoherent scattering background as well as the empty cell contribution.

3. Results

Let us consider first the preparation concentration, that is, a monomer volume fraction $\phi \sim 0.1$. In Figure 1, the scattering from the gel and from a semidilute solution of the same concentration is plotted. It is observed that the gel exhibits a large excess of scattering intensity with respect to the solution for almost the full range of the scattering amplitude, q, explored here. Consider the variation of $S(q)$ beginning from large q values to small q values. At large q values, the signal from the gel nearly meets that of the solution, but as q decreases, it shows a fast intensity increase, not present in the statistical gels. Note that in this q regime, a slight upward concavity may be seen. This increase is followed by a strong "shoulder" at intermediate values of the scattering vectors, which is more sudden than the slope variation of the semidilute solution around $1/\xi_{\mathrm{sol}}$, which is Lorentzian-like in this q range. Finally, for the gel, one observes again a strong increase of intensity at about 10^{-2} Å^{-1}. A similar increase at small angles can also be observed for the statistical gels of ref 5 and semidilute solutions, but only at higher polymer concentrations and at much smaller q values. This "stray" scattering in solutions is called the Picot–Benoît effect,[13] but its physical origin is still unclear. In the same q range as in Figure 1, both the shoulder and the strong increase in intensity are absent in the scattering function of statistical gels.[5] The scattering by statistical gels can be described using an Ornstein–Zernicke function[9] in this q range. It is also evident from the figure that any attempt to extract directly a correlation length, associated with the length scale above which the gel is homogeneous, from those data is meaningless.

Let us now examine how the scattering intensity changes as the gel swells. The studied swelling ratios range from $Q_{\mathrm{prep}} \sim 10$ to $Q_{\max} \sim 23$ (here, $\phi = 1/Q$). In Figure 2a, the scattering intensity from the gel and from semidilute solutions at the same concentrations are displayed. For each swelling ratio, we have a pair of curves which present the same general features as the pair of Figure 1. Note however that, as the gel swells, the "shoulder" at intermediate q values becomes less sharp. The apparent position, q^*, associated with this shoulder does not change significantly with swelling ratio, it remains $q^* \simeq 4 \times 10^{-2}$ Å^{-1} for all swellings.

In Figure 2b, the normalized intensity defined as $I(q)/\phi$ is plotted versus q for different values of ϕ. Consider the solution curves. This set of curves has a fanlike appearance. At low q ($q\xi < 1$), the curves are well separated, while at larger q values ($q\xi > 1$), there is a strong tendency to overlap. This overlapping tendency reflects the fact that at large q values $I(q) \sim \phi q^{-5/3}$; that is, the signals from inside each blob ($q^{-5/3}$) are added together as for dilute objects. This asymptotic regime is not completely achieved in the q range of the figure, neither for the solutions nor for the gels. For the gels, at $q \geq q^*$, the normalized intensity exhibits a variation stronger than $q^{-5/3}$. The same overlapping tendency as that for the solutions is seen whereas the normalized intensity fans out at $q \simeq q^*$. Although the intensity $I(q^*)/\phi$ from the gel is stronger than the scattering at $q = q^*$ from the solutions, its dependence on ϕ is approximately the same as for the solutions. Around the shoulder, for scattering vectors in the range approximately given by 10^{-2} Å^{-1} $< q < 4.0 \times 10^{-2}$ Å^{-1}, the separation of the normalized intensity with decreasing ϕ is similar to that of the solutions. The solution-like behavior of the gel in this q range can be directly seen in Figure 3, where we plotted the variation of $I(q^* = 4 \times 10^{-2}$ Å$^{-1})$ with ϕ for the gel and the solutions.

In order to examine the strong scattering excess at small angles, another data set corresponding to smaller q values—D11 spectrometer data—is plotted in Figure 4 together with the D17 data of Figure 2. The swelling ratios are the same for both sets of data, and consequently, they are superimposable. At very small q, the intensity seems to be approximately described by a scattering law of the type $I(q) \sim \phi q^a$, where a is $\simeq -3$. However, the signals for different degrees of swelling are not exactly superimposed: it seems that the larger the degree of swelling, the

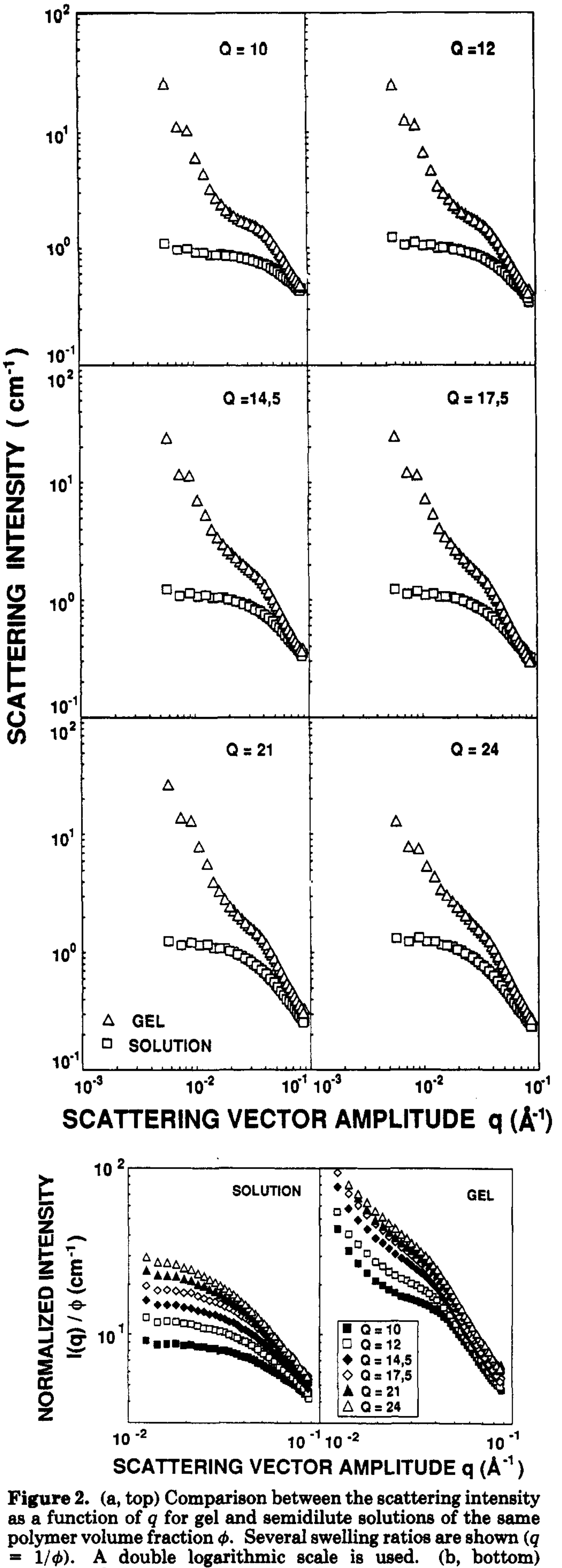

Figure 2. (a, top) Comparison between the scattering intensity as a function of q for gel and semidilute solutions of the same polymer volume fraction ϕ. Several swelling ratios are shown ($q = 1/\phi$). A double logarithmic scale is used. (b, bottom) Normalized scattering intensity $I(q)/\phi$ as a function of q for data of (a).

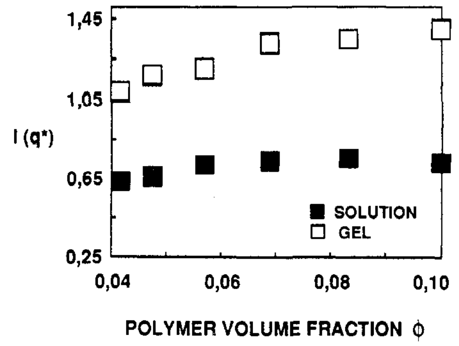

Figure 3. Variation of the absolute intensity at the shoulder position $I(q^* = 4 \times 10^{-2}$ Å$^{-1})$ with ϕ for the gel. The intensity $I(q^* = 4 \times 10^{-2}$ Å$^{-1})$ is also shown for a series of semidilute solutions of the same ϕ.

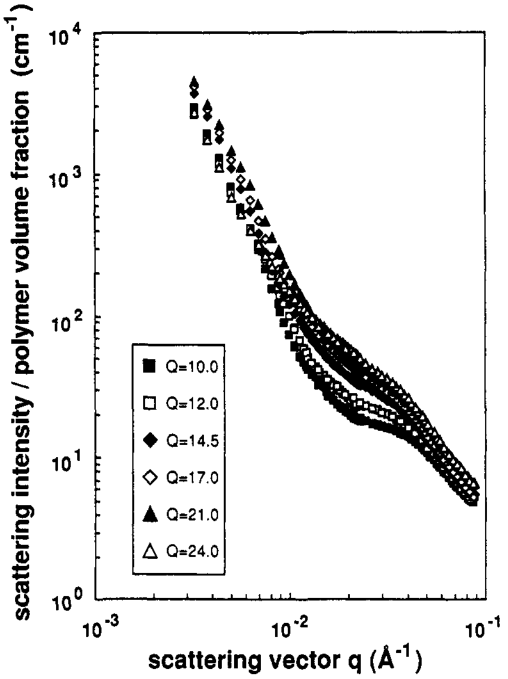

Figure 4. Normalized scattering intensity for the end-linked gel at different swelling ratios. A $\log(I(q)/\phi) \times \log(q)$ representation is used ($Q = 1/\phi$).

weaker the slope of the scattering intensity. In fact, $a \simeq -3$ is a mean apparent scattering law for this regime, whereas the signals for different degrees of swelling cross each other slightly.

4. Discussion

Classical theories describing chain behavior in gels can be roughly divided into two main approaches.[7,14] Earlier theories consider a competition between dilution of the network and elasticity of individual chains.[8] In this case, a significant stretching of individual chains is a constraint against infinite dilution of the polymer and it limits the maximum amount of solvent that a gel can absorb. Another more recent approach[9] stresses the role of the excluded volume interaction in gels (rather than the stretching). Under certain conditions, it was proposed that chains in a gel behave as in a semidilute solution, that is, a solution at a concentration $\phi > \phi^*$, ϕ^* being the minimum concentration at which elementary chains begin to overlap. In a semidilute solution, the correlations along one chain are screened out by the presence of neighboring chains *via* excluded volume interactions. Scaling arguments suggest that a single chain can be viewed as a collection of pieces of size ξ (blob) distributed in space as in a random walk problem. The screening length ξ is predicted to vary with polymer volume fraction as $\xi \sim \phi^{-3/4}$. The analogy between gel and semidilute solutions consists of considering a gel that can be synthesized at ϕ^*, which corresponds to the equilibrium swelling state. In this case, one should find for the gel a screening length ξ that depends on ϕ in the same fashion as in a semidilute solution. This approach thus explains, semiquantitatively, the behavior of the cooperative self-diffusion coefficient in gels.[15]

If one considers the main hypotheses of the theories mentioned above, it is possible to calculate the general features of the scattering at small angles for gels. We will focus on the upper limits for the scattering function, that is, the strongest scattering that can be found using such theories. Consider a gel synthesized by end-linking monodisperse chains of gyration radius R_g. The analogy between gel and semidilute solutions suggests that the scattering function at small angles ($q \leq 1/R_g$) from a gel should be of the Ornstein–Zernicke type for any concentration $\phi > \phi^*$. In reality, this is foreseen for a gel and a semidilute solution at $\phi = \phi^*$ and would remain valid for $\phi > \phi^*$, for a gel synthesized at ϕ^*. According to this picture,[9] the scaling behavior of the intensity, or the screening length, with the concentration, should be similar in gels and solutions,[16] that is, $I(q \to 0) \sim \phi^{-1/4}$ and $\xi \sim \phi^{-3/4}$. Thus, in this q range, the absolute intensity should have an upper limit equal to the scattering of a semidilute solution[7] presenting a screening length of the order of R_g, for $\phi \sim \phi^*$. For scattering vectors such that $q > 1/R_g$, the scattering should be ruled by the excluded volume behavior of the chains, and one should observe, in this regime, $I(q) \leq q^a$, with $a = -5/3$. This value is also an upper limit, since in older classical theories, chains are expected to be stretched through the swelling of the gel. This means that locally, inside the volume occupied by the chain, less matter would be present upon swelling and, consequently, the scattering intensity would exhibit a weaker variation with q than that of the solutions.

The experimental results presented in this paper do not agree with this picture. Contrary to those classical predictions, we observe that the scattering from the swollen gel at small angles ($q < 1/R_g$) is much stronger than that from the solution. (In the present case R_g of isolated precursor chains is about ~50 Å). This means that strong polymer concentration fluctuations in space are present on length scales larger than those associated with the mesh size. Even for $q \sim 1/R_g$, the scattering signal is still 2 times larger than the one from the semidilute solution at the same concentration. Therefore, even on those rather short length scales, the structure of the gel seems to be different from that of the solution.

Since the functionality of the junctions is not controlled by the chemistry of the reticulation process, we can consider that functionality is largely distributed in space with a mean value larger than that estimated previously (4–6). If sufficiently large nodules of DVB are formed during the synthesis, we could argue that branched structures, such as stars, microgels, and aggregates, could constitute the "basic objects" of the gel. The existence of such big objects in the reaction bath could lead to an intraparticle scattering larger than the one from a single blob in a semidilute solution of linear chains. But at smaller q, the scattering should be mostly governed by interparticle correlations between "basic" objects. The resulting spectrum could eventually present an intensity maximum if the "functionality" distribution of such objects was narrow enough and if a strong increase at small angles did not mask it. Indeed, maxima in end-linked gels swollen at swelling equilibrium have been observed in the past.[17]

In the case of a large polydispersity of the objects, the maximum would be softened and shifted. The new value depends on the cutoff (upper) limit of the mass distribution. The existence of the strong increase at small angles also contributes to the formation of the shoulder. At the preparation concentration, $Q = 10$, the shoulder is located at $q \sim 4 \times 10^{-2}$ Å^{-1}. This value can be associated with a distance $1/q$ slightly smaller than R_g. This result is expected since the gel is not synthesized at ϕ^* but at $\sim 2.5\phi^*$. At this scattering vector, the absolute intensity scattered by the gel is larger than the one from the solution, which can be obtained, for example, with compact starlike objects.[18]

When the gel is swollen from the preparation state, the apparent position of the shoulder does not change significantly. This may be due to the presence of the strong increase of the scattering at small angles that possibly masks the displacement of the shoulder. The variation of the intensity shoulder, $I(q^*)$, with ϕ is similar to the variation of the intensity at this q^* (chosen just for comparison) for the solutions, but with stronger absolute values. This suggests a classical behavior in swelling for those length scales.

The increase at small angles, described roughly by a q^{-3} law, suggests that a second type of structure is present at very large scales, orders of magnitude larger than the correlation length of the equivalent solution. Thus, the distribution in space of what we called above the "basic objects" is not homogeneous. The interpretation of the apparent slope $\simeq -3$ at small angles, which seems to decrease slightly with swelling,[19] is limited by the q range accessible in the experiment. For a complete characterization of this "superstructure", it would be necessary to extend these experiments to a smaller q range. At the present time, it is not possible to infer from the data whether smaller angles would reveal a saturation of the increase at small angles (in a log scale) or a maximum of the scattering at finite scattering vector.

Recently, it was proposed[20,21] that the scattering intensity of swollen gels could be decoupled in two parts. The total scattering intensity is then written as a sum of a static contribution due to large scale heterogeneities and a dynamic part, which is represented by an Ornstein–Zernicke function. Thus, the total scattering intensity is written

$$I(q) = I_{\mathrm{G}}(0)\exp(-\Xi^{s}q^{s}) + \frac{I_{\mathrm{L}}(0)}{1 + \xi^{2}q^{2}}$$

In this picture, Ξ represents the mean size of the heterogeneities, and ξ, the characteristic length scale of the dynamic fluctuations. It was shown that the value of $I_{\mathrm{L}}(0)$ and ξ may be different in a gel and in a semidilute solution of the same concentration. This procedure was carried out for gels which present scattering intensities that can be unambiguously decomposed in two contributions of distinct characteristic lengths (Ξ, ξ).[20] This was also applied to gels exhibiting smooth scattering functions where $I_{\mathrm{L}}(0)$ was determined independently by osmotic and shear moduli measurements.

If one tries to fit the spectra presented above with the same procedure, one finds that it is not possible. The Lorentzian function is smoother than the observed shoulder. This shoulder is most likely a hidden maximum which needs to be fitted by a third curve centered at a finite value of q (e.g., $q = q'$). This would imply a fitting procedure with too many parameters.

Finally, if we compare the results described above to the ones from statistical gels of ref 5, we see that the concentration fluctuations (in space) in those systems are very different, despite the fact that both samples have approximately the same elastic modulus and equilibrium swelling ratio in a good solvent. In fact, this picture was recently pointed out by Vilgis who suggested that *small* concentration fluctuations[10] could be responsible for a strong difference in the small angle scattering without changing significantly the modulus, that is, the mechanical and swelling properties of the net. However, the above results suggest the existence of very strong concentration fluctuations in space in these end-linked gels, much stronger than the ones considered in ref 10.

5. Conclusion

We have compared the small angle neutron scattering from end-linked gels with that from semidilute solutions at the same concentration (the whole solvent being labeled with respect to the polymer). The gels exhibit an excess of scattering with respect to the solutions at all length scales such that $q\xi_{sol} < 1$, where ξ_{sol} is the correlation length associated with the solution. At intermediate q values ($q > 10^{-2}$ Å^{-1}), the scattering from the gel seems to be very different from an Ornstein–Zernicke scattering function, contrary to the case for low-functionality polystyrene gels such as statistical gels[5] (functionality = 4) and end-linked polystyrene gels (functionality = 3).[14] The scattering function presents a "shoulder" at intermediate q values. The apparent position of the shoulder depends weakly on the degree of swelling, and it remains at $q^* \simeq 4 \times 10^{-2}$ Å^{-1}. The variation of $I(q^*)$ with the degree of swelling is similar to that found in the solutions, for the same value of q, but the absolute value is stronger. Finally, at small values of q a strong increase in intensity is observed with a dependence roughly equal to ϕq^{-3}.

The following picture for the structure of those gels is therefore suggested: the gel is a three-dimensional net built up from "basic objects" (like star molecules) with a rather large size distribution. In addition, these objects seem to be heterogeneously distributed in space, hence the strong increase in scattering at small angles.

The above results suggest that high-functionality gels exhibit a very different "structure" if compared to low-functionality gels. More data are, nevertheless, needed, and it should be interesting to study the structure of gels synthesized from very high functionality star polymers. We are planning to carry out such studies in the near future.

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