Soft Order in High-Functionality Star Polymer Solutions and Gels: A Small Angle Neutron Scattering Study

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ABSTRACT: Solutions of star-shaped molecules, and a gel synthesized by cross-linking the stars by the ends of their arms, have been studied by small angle neutron scattering (SANS). The polystyrene stars were synthesized using the so-called "core-first" method. As generally believed, this method gives rise to stars having quite monodisperse arms ($M_w \sim 20\,000$, in the present case) but with a rather large functionality distribution. Fractions of different average functionality, f, were diluted in a good solvent at a concentration $c = 50.0$ mg/cm^3. The fractions exhibit a pronounced intensity maximum in the scattering spectra, at the position q^*, and it was found that $I(q)^* \sim f^{0.85}$ and $I(q \to 0) \sim f^{0.75}$. In the case of solutions of polydisperse stars, the maximum of intensity is softened by the broad functionality distribution. The position of the maximum in this case varies with polymer volume fraction, ϕ, as $q^* \sim \phi^{0.42}$, whereas the strong dependence of $I(q^*)$ with ϕ cannot, however, be represented by a simple power law in the wide range of ϕ studied here ($0.03 < \phi < 0.33$). The gel synthesized by end-linking the polydisperse stars was also studied as a function of ϕ and its scattering compared to that of the solutions of polydisperse stars, at the same ϕ. For all of the studied concentrations, the scattering from the gel is superimposable on that from the solutions for all $q \geq q^*$. For $q < q^*$, the two scatterings are still perfectly superimposable for $\phi > \phi_{\text{prep}}$, which corresponds to a deswelling of the gel with respect to the preparation polymer volume fraction, $\phi_{\text{prep}} = 0.1$. A "network effect" is observed only for the swelling of the gel, $\phi < \phi_{\text{prep}}$, in the form of a scattering excess with respect to that of the solution. It is attributed to unfolding of heterogeneities, frozen by the cross-linking of the arms of the stars at larger scales than the stars size.

1. Introduction

Recently, the small angle neutron scattering (SANS) from different types of polymer gels, the solvent being labeled with respect to the polymer, has been studied as a function of the degree of swelling.[1-3] This gives information about the spatial concentration fluctuations and has been often compared to the scattering of linear chains of semidilute solution, taken as a reference system. At a given time, t, a snapshot of the semidilute solution can be represented by a kind of network with an average mesh size, ξ_{sol}, where ξ_{sol} is the screening length of the solution or the "blob" size of the system. It was shown that polymer gels present, in general, an excess of scattering at small angles compared to the "reference" semidilute solutions of linear chains at the same concentration. Such a scattering excess is attributed to "frozen" concentration fluctuations present in the gel on length scales which are larger than the blob size of the reference solution at the same concentration. In the present paper these concentration fluctuations are referred to as heterogeneities.

Two classes of heterogeneous gels, according to their SANS scattering intensities, can be defined from these SANS experiments.[4] A type 1 gel presents the following characteristics in its SANS spectrum:

(i) The scattering spectrum exhibits rather smooth variations in a logarithmic representation with a saturation at small q—if one neglects the possible anomalous increase of intensity at very small q, known as the Picot–Benoît[5] effect, which is also observed in the spectra of semidilute solutions. In addition, no intensity maxima are observed in the scattering of these gels. In many cases the data can be fitted well by an Ornstein–Zernicke function at small q and it is possible to derive a screening length, ξ_{gel}, from the scattering profile.[6,7]

(ii) When swollen with respect to the preparation conditions, the gel scatters at small angles a stronger signal than that scattered from a semidilute solution of the same concentration.

(iii) At the preparation concentration, the scattering signals from gel and semidilute solution are almost the same, provided the cross-linking ratio is sufficiently small.

(iv) The variation of ξ_{gel} with polymer volume fraction, ϕ, seems to be of the power law type: $\xi_{\text{gel}} \sim \phi^{\alpha}$, where the exponent α is systematically found to be stronger for these gels than for the semidilute solutions ($\alpha_{\text{sol}} \sim -0.77$). A typical value observed for the gels is $\alpha_{\text{gel}} \sim -1.7$, although it can be lower for weaker cross-link ratios.

A type 2 gel, however, presents the following characteristic spectra:

(i) Usually, at the preparation concentration, a very large scattering excess with respect to the reference semidilute solution is already present in a wide range of scattering vector amplitudes.

(ii) At low q, one often observes a very strong dependence of the scattering intensity on q, very different from an Ornstein–Zernicke function and from the Picot-Benoît effect of semidilute solutions.[2] As a result, no correlation length can be extracted from this part of the spectrum using the available spectrometers.

(iii) At intermediate q values ($q \sim 0.01$ Å^{-1}) the structure factor of the gel often exhibits a sudden change

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of slope in a log–log plot (a shoulder), or even a maximum.[8] The shoulder characterized by its position q^* and its height $I(q^*)$ can be viewed as the convolution of the steep increase observed at low q and a soft maximum at intermediate q values. It is very likely that the two parts of the spectrum have different physical origins.

With type 1 are usually associated low-functionality gels. For instance, gels formed by random cross-linking of very long linear chains in semidilute solutions[1] (functionality, $f = 4$), referred to as statistical gels, belong to this family. Some model networks prepared by end-linking[11,12] of monodisperse chains with cross-linkers of functionality $f = 3$, referred to as low-functionality end-linked gels,[13] also demonstrate type 1 characteristics. The results for statistical gels are explained in semiquantitative terms by a model which maps the cross-linking of a semidilute solution on a percolation of blobs problem.[14] In this model, regions rich in cross-links (hard zones) are separated from each other upon swelling and the measured screening length, ξ_{gel}, is related to the size of larger softly cross-linked "pouches" formed by the spatial separation of such hard regions. Similar results found for low-functionality end-linked networks are qualitatively interpreted in the same fashion: the random distribution of cross-links and entanglements in space is responsible for the formation of heterogeneities after swelling.[11,12]

Gels made by anionic copolymerization of styrene and divinylbenzene (DVB) molecules[2] are associated with type 2. In reality, these are also gels made by end-linking α,ω-difunctional monodisperse chains. The bridging units (DVB) can polymerize between themselves, preventing a chemical control of functionality, contrary to the low-functionality end-linked gel mentioned above. In the present paper, this system is called uncontrolled-functionality end-linked gel. Recent SANS studies on these systems[2] suggest that they are made of "objects" rich in cross-linked poly-DVB, such as star-branched polymers. These objects would be responsible for the shoulder observed at intermediate q values. As a matter of fact, earlier work on star solutions synthesized in similar conditions[15,16] exhibited a maximum in the scattering intensity at comparable q values. These experiments, together with some theoretical predictions on star-shaped polymers in solution,[17,18] suggest that, if the functionality is sufficiently large, concentration fluctuations due to the packing of stars in space can be present in semidilute solutions and gels.

The experimental approach used in earlier works[1,2] for the study of large-scale concentration fluctuations in low-functionality gels was aimed at the comparison between the scattering from gels and semidilute solutions of linear chains at the same concentration. As should be evident below, it is more convenient to compare the scattering from high-functionality gels with that from semidilute solutions made of (precursor) star-shaped polymers rather than with the scattering from linear chains: the former can exhibit a spatial order before cross-linking, which is not present in solutions of linear chains. This approach has led to a brief SANS study of correlations in star solutions, similar to recent parallel studies.[15,16] In Figure 1, the general procedure used here is represented schematically. In step 1, stars with a broad distribution in functionality are prepared with the core-first method.[19] From this precursor solution of stars, three different portions are separated. The polymers of portion 1 are separated in different fractions of different molecular weights. Each fraction will be studied at a fixed concentration of 50 mg/cm^3. Portion 2 is kept as a precursor solution with respect to the reticulation process that is carried out with the star molecules of portion 3. The resulting network obtained from cross-linking the stars is referred to as gel of end-linked stars.

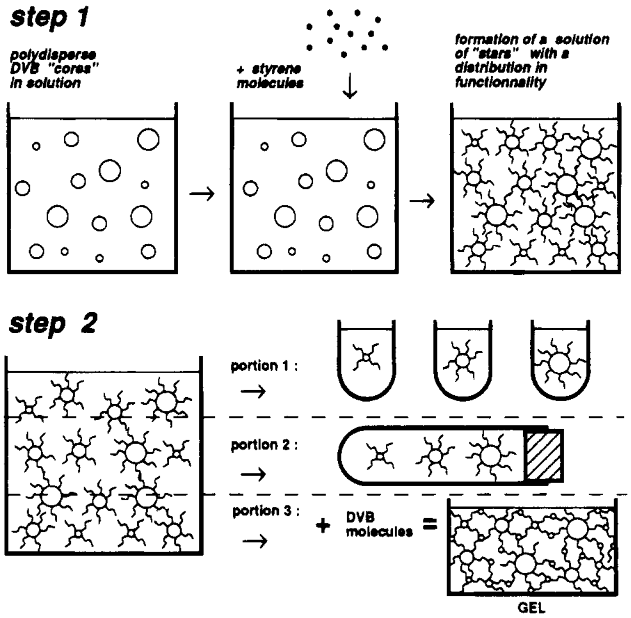

Figure 1. Schematic representation of the synthesis of the solutions and gel studied in this paper. Step 1: (a) Formation of reactive polydisperse divinylbenzene (DVB) cores in solution; (b) addition of styrene monomers; (c) formation of star polymers with a broad distribution of functionality. The outer ends of the arms of the stars are still reactive (see Experimental Section). Step 2: (1) Part of the star polymers obtained at the end of step 1, portion 1, are extracted from the reacting vessel. The reactive star outer ends are killed, and the stars are separated into fractions of different average functionalities. The scattering from each fraction is carried out at a fixed concentration of 50 mg/cm^3. (2) Part of the star polymers obtained at the end of step 1, portion 2, are extracted from the reacting vessel. Their reactive outer ends are killed, and they are kept polydispersed. A study of these polydisperse stars, as a function of the polymer volume fraction, is carried out. (3) DVB molecules are added to the rest of the reactive polydisperse stars, portion 3, which gives rise to a gel. A study of the scattering of the gel is carried out as a function of the polymer volume fraction.

2. Experimental Section

Sample Preparation. In the first step of the so-called core-first method,[19] high-functionality branched objects are grown from poly(divinylbenzene) (DVB) cores obtained upon reaction with potassium naphthalene in tetrahydrofuran (THF) at −70 °C. The resulting nodules have a large molecular weight distribution and, consequently, also broad distribution in functionality. Styrene molecules are then added to the solution. The polystyrene arm molecules grown from the active DVB cores[19] are expected to be almost monodisperse since they are grown by anionic polymerization. An average molecular weight, M_n 20 000, is calculated from the ratio of converted monomer to potassium concentration.

In a second step, DVB is added to the living solution in the proportion of one DVB molecule to two expected living ends of polystyrene branches. This end-linking of the outer end of the branches of the star molecules forms a gel.

After gelation, the gel was washed in THF, to remove the extractable fraction of soluble material, and then dried, cut, and polished into disks. Each dried disk was swollen in deuterated commercial toluene to fit perfectly the neutron scattering quartz cell (1.50 mm × 1.0–3.0 mm).

Prior to cross-linking, a portion of the solution was extracted from the vessel and killed with methanol, for purposes of characterization. Some of these "precursor stars" were also diluted at different concentrations in toluene as the swollen gel, to carry out a comparative study between the gel and the solutions of stars. Another portion of the precursor solution was further fractionated into even smaller fractions of much more monodisperse stars. A solution of 50.0 mg/cm^3 in deuterated toluene was prepared from the material of each fraction.

SANS. Neutron scattering experiments were carried out at Laboratoire Léon Brillouin (LLB Saclay) using the spectrometer PACE at the following configurations: sample-detector distance d = 4.59 m with incident wavelength λ = 8.3 Å; d = 4.51 m and d = 1.51 m with λ = 8.16 Å. The incident beam diameter was 7 mm. A collimation of diameter 10 mm was positioned at distance $d_c - d$ before the sample. Standard procedures of data treatment were used, such as detector normalization with the flat incoherent scattering of water at the same experimental conditions. The absolute coherent scattering intensity was obtained by subtracting the appropriate incoherent scattering background, which changes with polymer concentration.

3. Sample Features

Some physical aspects of this cross-linking process are important for a correct understanding of the scattering properties of the systems studied. First, when stars are cross-linking at their outer ends, two (or more) arms of the same molecule may be attached by their ends. This leads to a decrease in the efficiency of the cross-linking process and possibly gives rise to more compact stars. Second, the DVB molecules used as coupling agent can also polymerize among themselves. This could create secondary nodules in between the ones generated in the first step. For the same reasons as in the first step of the synthesis, the formation (and functionality) of these second-step nodules cannot be chemically controlled. However, one expects the size of these nodules to be considerably smaller than those formed in the first step, since the quantity of DVB used in the second step is much smaller than that used in the first. The influence of the second-step nodules on the scattering will be discussed in the following section.

An additional property of the precursor stars, obtained by the core-first method, is their large functionality distribution.[20] Small and high molecular weight objects are present in the solution prior to cross-linkings, as was shown by gel permeation chromatography (GPC) coupled to light scattering measurements, performed on various fractions of the precursor molecules. An average functionality of each fraction can be obtained by dividing the average molecular weight (in weight) of a given fraction (obtained by light scattering) by the calculated molecular weight of one branch ($M_n \sim$ 20 000, see above). As a result, we find functionalities, f, ranging from 3 to approximately 100 for the star fractions. Throughout the paper, this average functionality will be used, but it must be stressed that the larger values of f are probably overestimated. Since linear chains are grown from sometimes massive DVB nodules, which are not necessarily spherical in shape, steric repulsion between monomers in the initial stages of polymerization could induce the formation of branches of higher mass than was calculated. Thus, the effective functionality would be smaller.

4. Results and Discussion

Consider the scattering of the different solutions. Each one of the fractions of the precursor solution was diluted in deuterated toluene and studied at the fixed concentration of 50 mg/cm^3. The mother solution of the polydisperse star polymers was studied at different concentrations in the semi-dilute regime. The results concerning solutions of star molecules are presented in the first part of this section. The scattering from gels obtained after crosslinking the polydisperse star solution as a function of polymer volume fraction, as well as a comparison between the scattering from the gel and that of the precursor star solution, is presented in the second part of this section.

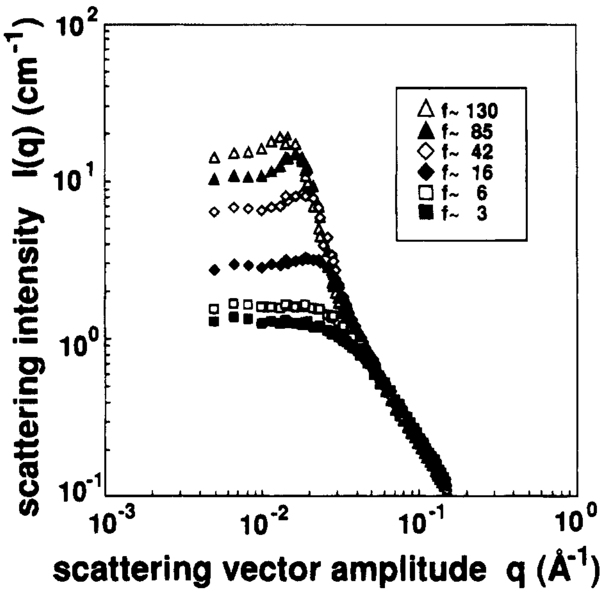

Figure 2. Scattering intensity as a function of the scattering vector **q** (in a log scale) for several fractions of stars prepared by the core-first method. The mean functionality associated with each fraction is shown in the legend, and they may be overestimated. Each solution is studied at a concentration of 50 mg/cm^3.

4.1. Scattering from Semidilute Solutions of Star Polymers. 4.1.1. Solutions of Fractionated Stars at the Same Concentration. The scattering from each mass fraction, as a function of the estimated functionality f, is presented in Figure 2. As stressed under Experimental Section, the average functionality of each fraction may be overestimated. The figure exhibits clear maxima for solutions of stars of estimated functionality greater than $f \approx 16$. Low-functionality star solutions do not present any maximum in the scattering spectrum, at this concentration, and the general shape of the scattering function, at small angles, is almost similar to that of linear chains.

Consider data as a function of the scattering vector amplitude q. Within the range $5.0 \times 10^{-2} < q < 10^{-1}$ Å^{-1}, most curves almost superimpose, but the higher the functionality f, the stronger the slight concavity in the scattering, in this log scale. For the solutions corresponding to functionalities of 6 and 3, there is no concavity: the scattering function, in logarithmic plot, is almost a straight line in this q range. The slope is -1.64, very close to the prediction for the scattering from a chain with excluded volume, which is $I(q) \sim q^{-5/3}$. This means that at these length scales, and at this concentration, the arms of the stars behave similarly to excluded volume linear chains.

At smaller q values, the scattering functions corresponding to different functionalities have rather different profiles. For solutions of stars low functionality (f = 3 and 6) the intensity starts to "saturate" (in this

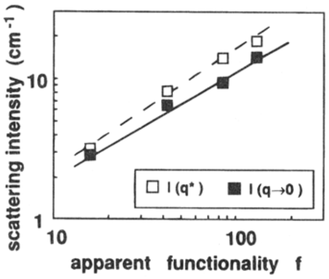

Figure 3. Intensity of the maximum $I(q^*)$ and intensity extrapolated to zero scattering vector, $I(q \rightarrow 0)$, for the solutions of Figure 1 as a function of the estimated functionality, f.

log representation) for $q \approx 5.0 \times 10^{-1}$ Å^{-1}; that is, they behave nearly as linear chains. In the case of solutions made of high functionality stars ($f \geq 16$), the intensity increases strongly with increasing functionality until a maximum is reached at $q = q^*$. For higher functionalities, we can associate an asymptotic slope $s \approx -3.8$ between the maximum of the scattering intensity and the value of $q \sim 5.0 \times 10^{-2}$ Å^{-1}. Such a scattering behavior, close to q^{-4}, may be due to a combination of factors: the stars can be viewed as "spherical brushes"[17] or, in other words, as nearly spherical objects with a high-density core and a very diffuse boundary. Moreover even after fractionation, they are still somewhat polydisperse. It is well-known that the form factor of compact and monodisperse spheres can be expressed as a q^{-4} law modulated by oscillations related to the size of the sphere.[21] In the present case, both the polydispersity and the fact that the boundaries are not sharp may account for the lack of oscillations.

The observation of a maximum for the higher functionality star polymers suggests a description in terms of spherical brushes which can intersperse to some extent, but, certainly, far less easily than linear chains. As a result, when the concentration is not too high, the "effective" excluded volume, v, of such objects should remain comparable with $4/3\pi$, R_g^3 (R_g being their radius of gyration). This is the same reason as that responsible for the observation of a maximum in the scattering profile by a system of weakly concentrated hard spheres.

For $q < q^*$, the intensity first decreases and then it seems to stabilize (in a log representation). This allows an extrapolation of $I(q)$ for $q \rightarrow 0$. The intensity at the maxima $I(q^*)$ and $I(q \rightarrow 0)$ varies with functionality. The values of $I(q^*)$ and $I(q \rightarrow 0)$ derived from Figure 2 are plotted in Figure 3 as a function of functionality. Both quantities increase with functionality for a mixed monomer concentration, the variation of $I(q^*)$ being stronger than that of $I(q \rightarrow 0)$. If the data are plotted in a logarithmic scale, as in Figure 3, $I(q^*) \sim f^{0.85}$ and $I(q \rightarrow 0) \sim f^{0.75}$. In a very dilute regime, one would expect a linear variation of $I(q \rightarrow 0)$ with f, that is, with the average molecular weight of the stars. Here, the presence of interparticle correlations, which give rise to the maximum, can presumably account for a weaker apparent exponent.

4.1.2. Solution of Polydisperse Stars.

The polydisperse star solutions are prepared from the precursor molecules which were used in the synthesis of high-functionality gels. Several spectra are shown in Figure 4 for different polymer volume fractions, ϕ, in $\log(I/\phi) \times \log(q)$ representation. They present, at first sight, the same basic features as observed in the fractionated case. At large q values, the scattering again seems to follow asymptotically a power law with a slope very close to -1.6, followed by a maximum at intermediate q values. Contrary to the fractionated stars, the intensity between the large q regime and q^* (maximum position) does not present a slope close to -4. It seems that the polydispersity in the size of the DVB cores and, consequently, in functionality is responsible for a softening of the maxima. The dependence with q, in this q range, is stronger than $q^{-1.6}$, and it varies slightly with concentration.

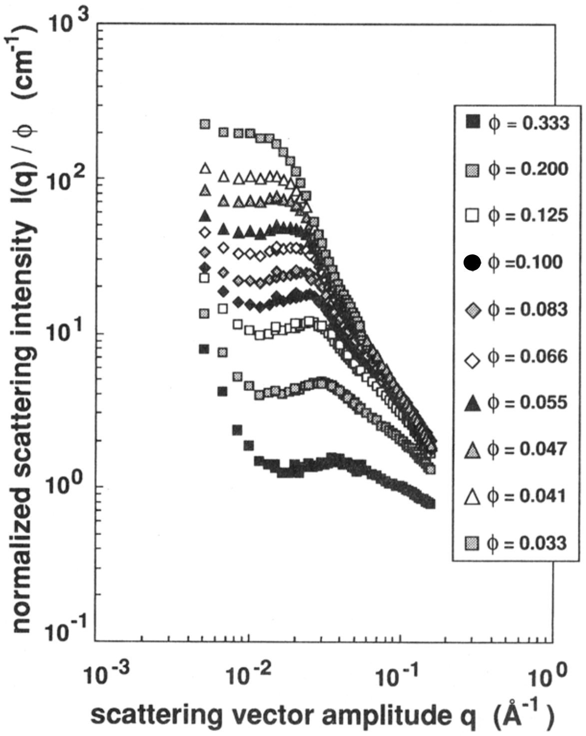

Figure 4. Scattering intensity, $I(q)$, as a function of the scattering vector, **q**, for several solutions of polydisperse stars. Data are plotted in a log $(I(q)/\phi) \times \log(q)$ representation, where ϕ is the polymer volume fraction.

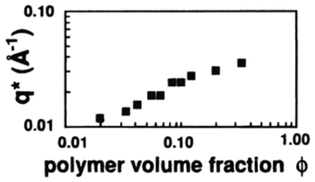

Figure 5. Variation of the position of the intensity maximum, q^*, as a function of the polymer volume fraction, ϕ, for the solutions of polydisperse stars of Figure 4. A logarithmic scale is used.

The variation of $I(q^*)$ and q^* with ϕ is plotted in Figures 5 and 6. Data of Figure 5 can be described by a power law, and $q^* \sim f^{0.42}$. For $I(q^*)$, the data cannot be represented by a straight line on a logarithmic scale. For the larger concentrations ($Q \leq 8$, $\phi \geq 0.125$) the dependence seems to approach a scaling law $I(q^*) \sim \phi^{-1}$. Such a behavior may be compared to the dependence $I(q \rightarrow 0) \sim \phi^{-1}$ for linear chains in the truly concentrated regime. For smaller concentrations, the dependence deviates strongly from this law with downward curvature. Note that for $Q \geq 24$ ($\phi < 0.042$) the maximum is practically transformed into a shoulder. The position of the shoulder is then taken for q^*. The transformation of the intensity maximum into a shoulder possibly indicates the approach of the overlap concentration, c^*, of the polydisperse assembly of stars. Before decreasing upon dilution for $\phi > \phi^*$, $I(q \rightarrow 0)$ should first saturate

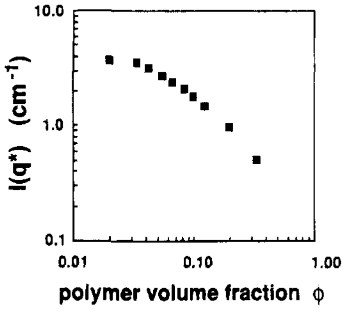

Figure 6. Variation of the intensity of the maximum, $I(q^*)$, as a function of the polymer volume fraction, ϕ, for the solutions of polydisperse stars of Figure 4. A logarithmic scale is used.

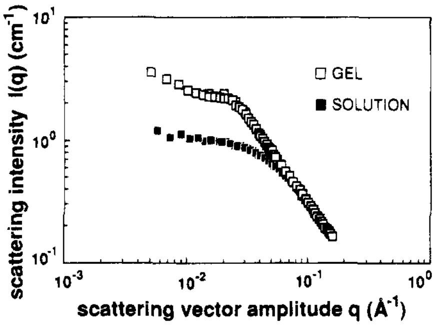

Figure 7. Scattering intensity, $I(q)$, as a function of q, for a gel of end-linked stars. A semidilute solution of linear chains at the same concentration is also shown. The swelling ratio is $Q = (V/V_{\mathrm{dry}}) = 12$.

at $\phi \approx \phi^*$. The tendency to a saturation of $I(q^*)$ at low ϕ in Figure 5 is therefore also consistent with the approach of ϕ^*.

Finally, it is important to stress that for the higher concentrations, on going to very small q values, a strong upturn is observed. This anomalous scattering is also present in semidilute solutions of linear chains, where it is known as the Picot–Benoît effect.[5] The upturn is visible for $q < q_{\mathrm{PB}}$ where q_{PB} increases with both molecular weight and concentration. The theoretical interpretation for this phenomenon is still an open question, and this type of effect should also be present in the spectra of fractionated stars if they are sufficiently concentrated. Because of this anomalous scattering at small angles, an extrapolation of $I(q \rightarrow 0)$ is very difficult to obtain.

4.2. Scattering from Gels Made from High-Functionality Polydisperse Stars Polymers. 4.2.1. Comparison with a Solution of Linear Chains. We will first use, for completeness, the procedure used by us for other gels[1,2,6,7], that is, the comparison between the gel and a semidilute solution of linear chains, at the same concentration. The swelling ratio is $Q = 12$, which is very close to the preparation concentration ($Q_{\mathrm{prep}} \sim 10$). As shown in Figure 7, the gel scatters a large excess, at small angles, with respect to the solution and it presents at intermediate q values a soft maximum in the scattering function, comparable to the solution of polydisperse star polymers. Such a maximum, not present in the spectra of type 1 gels, resembles the shoulder observed in the scattering of end-linked gels.[2] On the other hand, at larger q values, the scattering curves from the solution and the gel superimpose. Similar behavior was observed, as discussed in the previous paragraph, when the scatterings from solutions of stars polymers of different mean functionalities were compared.

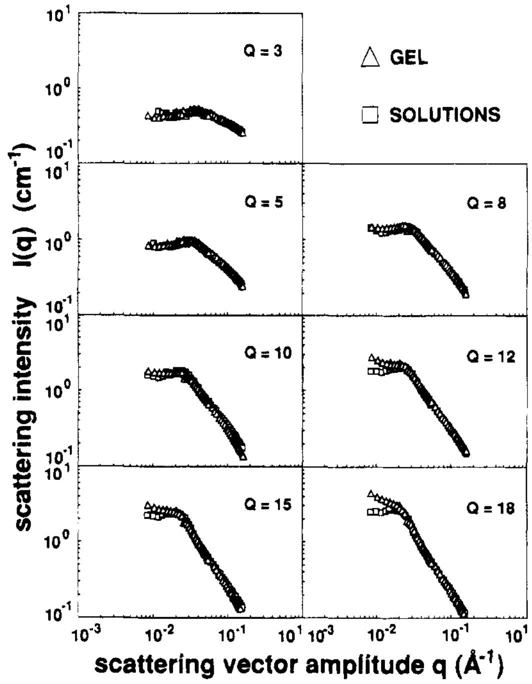

Figure 8. Scattering intensity, $I(q)$, as a function of q, for a gel of end-linked stars. Several values of the swelling ratio Q are shown ($Q = 1/\phi$). The scattering profiles from semidilute solutions of precursor stars, at the same concentration, are also plotted.

4.2.2. Comparison with a Solution of Star-Shaped Chains. In Figure 8 the scattering from the gel and that from its precursor solution are compared at different values of ϕ. For all ϕ, the scattering function from the gel presents an intensity maximum for intermediate values of the scattering vector **q** whose position and intensity are nearly the same as those of the solution. The scattered intensities from the gel and from the solutions are perfectly superimposable for $q > q^*$, which corresponds almost to a decade in q for the most swollen situation, $Q = 18$.

A difference between the spectra from gel and from the solution is observed for $q < q^*$, when $\phi < \phi_{\mathrm{prep}}$ ($Q > Q_{\mathrm{prep}}$). This difference consists of a scattering excess from the gels with respect to the solutions and increases as ϕ decreases. Although the shape of the scattering curves is very different, this increasing difference with the swelling degree resembles the behavior of type 1 gels. As proposed for these latter systems, such a scattering excess can be associated with heterogeneities in crosslink density on scales larger than the size of the "fundamental unit" of the system, believed here to be the star. This analogy to the picture of statistical gels[1] would suggest that the random aspect of the crosslink process could be responsible for the formation of heterogeneities, which could be revealed by swelling and which would give rise to a scattering excess at small angles. For swelling ratios smaller than $Q = 10$, the system is submitted to an opposite situation: deswelling with respect to the preparation conditions. But in this case, no scattering excess with respect to the solution is observed. This suggests that when the gel is deswollen, the stars are able to pack or intersperse in the gel, in the same manner as they do in solution. They do not "feel" very strongly the presence of the cross-linking points introduced in the second step of the cross-link process. In fact, the presence of those cross-links which end-link the stars can only be seen indirectly, by the swelling of the gel with respect to the preparation state.

Very likely, the latter do not consist of nodules as large as the cores of the stars.

Finally, let us compare the results obtained in this paper with previous results regarding other polymer gels. First of all, we can classify the gel of end-linked stars studied here as a type 2 gel. It shows a strong excess scattering at small angles if compared to a semidilute solution of linear chains at the same concentration. It also exhibits either a maximum in scattered intensity or a shoulder, the latter being very similar to the one observed for end-linked gels of uncontrolled functionality.[2] It was shown that those end-linked gels present a very strong upturn in the scattering intensity at very small angles,[2] where $I(q)$ varies roughly as $\sim q^{-3}$ (for any polymer concentration). Such an upturn probably masks a maximum of intensity which would transform it into a shoulder. For the gel studied here, no data are available at a very small q range. Therefore, the increasing difference between the spectra from the gel and the solution, with increasing swelling ratio, also transforms the maximum into a shoulder as shown in Figure 8.

5. Conclusions

It was shown, using SANS, that high-functionality star polymers, in semidilute solutions as well as end-linked to form a gel, exhibit a soft order. The scattering spectra exhibit an intensity maximum $I(q^*)$ at q^*, the value of which depends on the functionality of the stars, f. In the case of fractionated species of average functionality f, the intensity at the maximum varies as $I(q^*) \sim f^{0.85}$. For the zero q limit, we find $I(q \rightarrow 0) \sim f^{0.75}$. These power laws are obtained for a fixed polymer concentration of 50 g/cm^3 for polystyrene stars in deuterated toluene.

In the case of polydisperse solutions of stars, an intensity maximum is also observed but appears to be softened by the polydispersity effect. A gel made by the end-linking of the same polydisperse stars exhibits the same kind of scattering spectra. With both systems, gel and solutions, one can associate the same power law $q^* \sim \phi^{0.42}$ for the variation of the position q^* of the maximum with polymer volume fraction, ϕ. The strong dependence of $I(q^*)$ with ϕ cannot be represented by a simple power law.

For all swelling ratios the signal scattered from the gel is perfectly superimposable on that from the solutions for $q > q^*$. It is only for $q < q^*$ that differences between the scattering of the gel and that of the solutions of stars are observed. A scattering excess in the case of the gel is visible only when $\phi < \phi_{\text{prep}}$, and it may be attributed to the formation of heterogeneities on length scales larger than the size of the precursor stars. Conversely, for $\phi > \phi_{\text{prep}}$, the spectra from the gel and from the solution are practically identical. In other words, within the precision of the experiment, no network effect is visible in deswelling with respect to the preparation state ($\phi > \phi_{\text{prep}}$). On the other hand, some network effect is observed in the case of swelling with respect to the preparation conditions ($\phi > \phi_{\text{prep}}$), but it corresponds typically to length scales larger than the size of the precursor stars.

Finally, these studies support recent conclusions about the structure of end-linked gels synthesized by block copolymerization of nearly polydisperse polystyrene chains and divinylbenzene molecules.[2] The spectra of those systems exhibit a shoulder, which was interpreted as a consequence of the high average functionality of the junctions, in accordance with the present results.

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References and Notes

(1) Mendes, E.; Lindner, P.; Buzier, M.; Boué, F.; Bastide, J. *Phys. Rev. Lett.* **1991**, *66* (12), 1595.

(2) Mendes, E.; Girard, B.; Buzier, M.; Boué, F.; Bastide, J. *Macromolecules* **1993**, *26*, 6873.

(3) Mallam, S.; Horkay, F.; Hecht, A. M.; Geissler, E. *Macromolecules* **1989**, *22*, 3356.

(4) The classification scheme presented in this introduction considers the small survey on polymer gels that exists at the present.

(5) Benoît, H.; Picot, C. *Pure Appl. Chem.* **1966**, *12*, 545. At very small q values ($q \leq 5-6 \times 10^{-3}$ Å^{-1}) there is sometimes an upturn in the scattering intensity from the gels which is comparable to that observed for semidilute solutions in the same range of q values. In the latter case, the phenomenon is often called the "Picot–Benoît" effect, but it has not received, as far as we know, a satisfactory explanation. The data points corresponding to this upturn are not taken into account in the determination of ξ either in the case of the solutions or in the case of the gels.

(6) For some gels, some authors proposed to fit the small angle signal range with the three parameter function $I(q) = A\,\exp(-q\xi)^{\beta}$, which also leads to a sort of correlation distance Ξ. See for instance ref 3 and: Horkay, F.; Hecht, A. M.; Mallam, S.; Geissler, E.; Rennie, A. R. *Macromolecules* **1991**, *24*, 2896.

(7) Shibayama, M.; Tanaka, T.; Han, C. *J. Chem. Phys.* **1992**, *97*, 6829.

(8) Duplessix, R. Thèse d'Etat, Université Louis Pasteur, Strasbourg, France, 1975.

(9) Benoît, H.; Decker, D.; Duplessix, R.; Picot, C.; Rempp, P.; Corron, J. P.; Farnoux, B.; Jannink, G.; Ober, R. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 2119.

(10) Polydimethyl siloxane rubbers cross-linked in bulk by γ-irradiation behave in the same manner when swollen in good solvent. See: Mendes, E.; Hakiki, A.; Ramzi, A.; Herz, J.; Schosseler, F.; Munch, J. P.; Boué, F.; Bastide, J. *J. Polym. Mater. Sci. Eng.* **1993**, *68*, 231.

(11) Mendes, E. Thesis, Université Louis Pasteur, Strasbourg, France, 1991.

(12) Hakiki, A. Thesis, Université Louis Pasteur, Strasbourg, France, 1991.

(13) With this class are also associated gels which are made by radical copolymerization of poly(methyl methacrylate). It is possible to fit data with an Ornstein–Zernicke function and to obtain a correlation length. The scattering intensity in the preparation state is, nevertheless, much larger than that of an equivalent semidilute solution. See: Lal, J.; Bastide, J.; Bansil, R.; Boué, F. *Macromolecules* **1993**, *26*, 6092.

(14) Bastide, J.; Leibler, L. *Macromolecules* **1988**, *21*, 2648.

(15) Richter, D.; Jucknischke, O.; Willner, L.; Fetters, L. J.; Lin, M.; Huang, J. S.; Roovers, J.; Toporowski, P.; Zhou, L. L. *ACS-PMSE, Symposium on Neutron Scattering from Polymers*; American Chemical Society: Washington, DC, 1992.

(16) Dozier, W. D.; Huang, J. S.; Fetters, L. J. *Macromolecules* **1991**, *24*, 2810.

(17) Daoud, M.; Cotton, J. P. *J. Phys.* **1982**, *43*, 531.

(18) Witten, T. A.; Pincus, P. A.; Cates, M. E. *Europhys. Lett.* **1986**, *2* (2), 137.

(19) Rein, D.; Rempp, P.; Lutz, P. *J. Makromol. Chem., Makromol. Symp.* **1993**, *67*, 237.

(20) In fact, we do not know if the objects obtained in the first step are really spherical in shape. The larger ones should be thought as polymer-enveloped colloidal particles, which are referred to as "stars" throughout this paper for simplicity.

(21) Higgins, P.; Benoît, H. In *Polymers and Neutron Scattering*; Oxford University Press: Oxford, U.K., 1993.

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