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Swelling and cross-linking density effects on the structure of partially ionized gels

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Résumé. — Nous étudions par diffusion de neutrons aux petits angles des gels faiblement ionisés à taux de réticulation et gonflement variables ainsi que les solutions équivalentes. L'excès d'intensité diffusée par les gels par rapport aux solutions correspondantes est attribué à des fluctuations de concentration gelées qui sont associées à des régions plus densément réticulées. La variation de cet excédent d'intensité avec le taux de réticulation ou le gonflement donne à ces régions l'image d'une structure plutôt compacte, différente des grandes structures ramifiées et enchevêtrées, suggérées pour d'autres gels. La présence d'interactions électrostatiques au cours de la gelification réduit de façon notable la taille et l'amplitude des fluctuations gelées.

Abstract. — We report on small angle neutron scattering experiments performed on weakly ionized gels at various cross-link densities or swelling ratios and on the corresponding solutions. The excess of scattering intensity observed in the gels compared to the equivalent solutions is attributed to frozen fluctuations of concentration associated with more densely cross-linked regions. The variation of the excess scattering intensity with cross-linking degree or swelling ratio supports the picture of a rather compact structure for these regions in contrast with the large branched overlapping structure suggested for other gels. The presence of electrostatic interactions during the gelation reaction reduces noticeably the extent and the amplitude of the frozen fluctuations.

Introduction.

Electrostatic interactions modify deeply the behaviour of polymer solutions even when the polymer chains are moderately charged. A few charges per chain are enough to dissolve in water polymers with an otherwise hydrophobic backbone [1]. Recently both theory [2, 3] and experiments [4] have shown that in such systems, when the solvent becomes poor enough, the interplay of hydrophobic and electrostatic interactions prevents macroscopic phase separation

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and favours the formation of microdomains richer in polymer. The enhanced fluctuations of polymer concentration with finite wavelength correspond to a maximum in the scattering intensity for non-zero values of the momentum transfer \( q \). This peak has been observed in the small angle neutron scattering (SANS) intensity measured on weak polyacids solutions [4] and the evolution of its position and intensity is satisfactorily predicted by the model [2, 3] as a function of ionization degree, solvent quality, polymer and salt concentrations.

Parallel SANS investigations on poly(acrylic acid) (PAA) gels in their reaction bath [5-7] have revealed the same basic features as for the solutions. Except for a small shift of the peak position to smaller momentum transfer values in the gels, no clear difference could be detected between moderately cross-linked gels and solutions in the same conditions. In particular, at small \( q \) values, the intensity scattered from the gels is only slightly higher than in the corresponding solutions. This difference between gels and solutions is more marked for higher cross-linking degrees but tends to vanish as the ionization degree increases [6, 7].

This behaviour can be compared with that observed on neutral gels which can exhibit, depending on the synthesis path and the swelling degree, large excess of scattering intensity relative to the corresponding solutions [8-13]. The origin of the larger fluctuations of polymer concentration in the gels is still a matter of debate [14, 15]. Whatever the mechanism for these increased fluctuations, the presence of electrostatic interactions was thought to hinder or even prevent them in charged gels because of the huge increase in the free energy associated with any large scale fluctuation in polymer concentration. Thus even weakly charged gels could be thought to be more homogeneous on large distance scales than neutral gels. Light scattering [6] and SANS [6, 7] have confirmed this view for moderately cross-linked gels in the reaction bath. However recently experiments have shown more evident differences between polyelectrolyte gels and solutions as cross-linking degree or swelling ratio increase [16]. This behaviour is consistent with the one observed with neutral systems [8-13] and expresses some rule of thumb that differences between gels and solutions are increasingly revealed as the swelling equilibrium of the gels is approached [16]. The distance to the swelling equilibrium can be reduced either by letting the gels swell or by increasing the cross-linking degree in the reaction bath. Both approaches are used in this paper to study charged gels that are closer to their swelling equilibrium.

In the following we compare weakly charged PAA gels and solutions by using the SANS technique. After describing the experiments, we report first on the effects of dilution on the solutions. In a second part the gels in the reaction bath with increasing cross-linking degree are compared with a solution at the same concentration. Then the intensity scattered from swollen gels with constant cross-linking degree is compared to the spectra obtained from dilute solutions at the same concentration. Finally, the influence of charges on the synthesis of the gels and solutions is illustrated before the summary and discussion of the results are presented.

Experimental part.

Sample preparation follows the procedure described elsewhere [4-7]. Solution samples are obtained through free radical polymerization of acrylic acid in D_2O. After careful bubbling of nitrogen through the monomer solution, the polymerization reaction initiated by ammonium persulfate (\( 2\, \% \text{ g/g} \)) proceeds for 12 h in an oven at 70 °C. Monomer concentration in the reaction bath is 0.08 g/cm^3 (\( C_p = 1.11 \, \text{M} \)). In this way, we obtain a stock solution that is used to prepare solutions with the desired polymer concentration and ionization degree \( \alpha \). The latter is fixed by adding the appropriate amount of sodium hydroxide (NaOH) to the solutions to shift the acido-basic equilibrium that governs the dissociation of the weak polyacid. Two neutralization degrees, defined as the molar ratio of sodium hydroxide to monomers, were used in this study: \( f = 0.05 \) and \( f = 0.10 \). The corresponding ionization degrees vary with
polymer concentration and are estimated to lie in the range 0.051-0.062 for \( f = 0.05 \) and 0.10-0.106 for \( f = 0.10 \) [4, 5]. It can be noted that the \( \Theta \) temperature for polyacrylic acid in \( D_2O \) is about 27 °C [17]. Therefore unneutralized PAA solutions tend to become cloudy and then separate into two phases at room temperature. Thus stock solution amounts to be neutralized were taken at about 40 °C with pipettes at the same temperature. After the neutralization the solutions remain clear and can be used at room temperature.

Gel samples are obtained by following the same lines as for solutions but adding to the monomer solution the appropriate amount of cross-linker, N-N' methylene bisacrylamide. The cross-linking degree \( r_c \) is defined as the molar ratio of cross-linker to monomer. Two different series of gels were prepared.

Gels studied in the reaction bath were synthesized directly into cuvette scattering cells (Hellma) with 5 mm optical path and the neutralization \( (f = 0.10) \) was performed before the polymerization reaction. The cross-linking degree \( r_c \) was varied between 0 and 0.05. Thus the sample with \( r_c = 0 \) was a solution synthesized in the presence of charges to be compared with the stock solution prepared with no charges and neutralized subsequently. Equilibrium swelling ratio for analogous gels prepared and swollen in \( H_2O \) is about 10 when \( r_c = 0.05 \).

Gels designed to be studied as a function of swelling ratio were prepared in the shape of thin slabs (2-5 mm thickness) inside a mould with no sodium hydroxide added. Cross-linking ratio was 0.01. After completion of the reaction, small disks of gels were cut from the slabs and weighed into small vessels. This step has to be done before the mould has cooled down to room temperature to prevent the deswelling of the gels below the \( \Theta \) temperature. Then the appropriate amount of NaOH and \( D_2O \) were added to the vessels to bring the gels to the desired swelling ratio and neutralization degree \( (f = 0.05 \) and \( f = 0.10 \). The gels were then allowed to take up the solvent and equilibrate in the tightly closed vessels for a few days. Swelling ratios were calculated to bring the gels to a final thickness equal to 5 mm, in order to fit scattering cells made by assembling two quartz plates and a 5 mm thick quartz ring spacer (Hellma). Thus the swelling ratio \( Q \) of the gels relative to the concentration in the reaction bath is fixed by the initial thickness of the slab. An additional value \( Q = 8 \) for the swelling ratio was achieved by letting a 2 mm thick gel swell to a 6 mm thickness. The corresponding scattering cell was built by adding a thin 1 mm ring to the 5 mm ring.

Solutions were diluted to the same concentrations as the gels to allow direct comparison and to minimize the number of background samples. Table I gives a summary of the samples with the corresponding swelling ratios. It must be noted that the neutralization of samples at the concentration of preparation was performed by using small amounts of concentrated NaOH.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Gels</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f = 0.05 )</td>
<td>( f = 0.10 )</td>
</tr>
<tr>
<td>S1f5</td>
<td>1.02</td>
</tr>
<tr>
<td>S2f5</td>
<td>1.95</td>
</tr>
<tr>
<td>S5f5</td>
<td>4.63</td>
</tr>
<tr>
<td>S8f5</td>
<td>8</td>
</tr>
<tr>
<td>S16f5</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Table I. — Characteristics of the swollen gels and dilute solutions. Swelling ratio \( Q \) is defined relatively to the concentration in the reaction bath \( C_p = 1.11 \) M.
solutions to limit the change in polymer concentration to an insignificant 5 %. To calculate the final concentrations, the difference in partial molar volumes between monomer and polymer was taken into account and total conversion was assumed. Errors in the final concentrations should be small and the same for both gels and solutions. Equilibrium swelling ratio in D$_2$O is close to $Q = 8$ (resp. $Q = 15.6$) for gels with $f = 0.05$ (resp. $f = 0.10$).

The measurement of incoherent scattering levels was performed by using monomer solutions as background samples. In order to allow accurate corrections, a number of these samples was prepared. In the case of the gels studied in the reaction bath as a function of cross-linking degree, background samples were monomer solutions with the same composition (including cross-linker) as the gels. Thus each gel had its own background sample. This was necessary since the incoherent scattering contribution from cross-linker is not negligible when $C_p = 1.11$ M and $r_c \approx 2$-%. For both dilute solutions and swollen gels, background samples were monomer solutions with corresponding monomer concentration and ionization degree. Thus the cross-linker incoherent scattering was not taken into account for the gels but since $r_c$ is only 0.01, the error is small and vanishes for low concentrations where the main contribution to incoherent scattering is due to D$_2$O. Although no measurable difference could be expected between samples according to neutralization degree, this point was checked and measurements confirmed that background samples with $f = 0.05$ and $f = 0.10$ have the same incoherent scattering within experimental error (see below). All background samples were measured in 5 mm optical path cuvette cells.

Measurements were performed on the PACE spectrometer in Laboratoire Léon Brillouin (').

The wavelength for the incident neutrons was set to $\lambda = 6.5$ Å and sample-detector distance was fixed to 3.00 m. This configuration allows $q$ values in the range $9.7 \times 10^{-3} < q (\text{Å}^{-1}) < 10^{-1}$. Here $q$ is the usual scattering wave vector defined by $q = 4 \pi / \lambda \sin (\theta / 2)$ where $\theta$ is the scattering angle. The temperature of the samples was regulated to $T = 19.5 \pm 0.5 \degree \text{C}$. In order to better appreciate background subtraction, data treatment was done in several steps. Raw data were first corrected for electronic noise. Then the contribution of an empty quartz cell was subtracted from all samples, including background samples, after taking into account their different transmissions. The result was then normalized by the optical path length and by the incoherent scattering from 1 mm H$_2$O, corrected for electronic noise and empty cell contribution. Finally the absolute total intensity was obtained by using the value 0.872 cm$^{-1}$ for the absolute incoherent cross section of H$_2$O in our experimental conditions [18]. In figure 1 are plotted the absolute incoherent cross section of the background samples as a function of their transmission. In a last step, these values had to be subtracted from the absolute total intensities scattered from the gel and solution samples to obtain their absolute coherent scattering intensities. This subtraction was done directly for dilute solutions and gels in the reaction bath. However, unlike these samples, the swollen gels had systematically lower transmissions than their corresponding background samples, thus arising questions about the accuracy of this last step for the swollen gels. This point will be addressed in detail below.

Dilute solutions.

Figure 2 shows the evolution with polymer concentration of the intensity scattered from the solutions with $f = 0.05$. These results cover a broader range in polymer concentration ($0.072 < C_p (M) < 1.1$) compared to a previous paper ($0.4 < C_p (M) < 1$) [4]. The qualitative behaviour remains the same as previously described.

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Fig. 1. — Absolute incoherent scattering intensity for the background samples as a function of their transmission. Solid line is a parabolic interpolation fit.

Fig. 2. — Evolution with polymer concentration of the intensity scattered from solutions with \( f = 0.05 \). Solid lines show the fits of the theoretical structure factor [2, 3] to the experimental data.

The scattering intensities show a maximum with position \( q^* \) shifting to smaller \( q \) values as \( \alpha \) and \( C_p \) decrease. This feature is consistent with the model of microphase separation that predict the following relationship [2, 3]:

\[
q^* \approx (48 \pi l_B / \alpha^2) \alpha \Phi_p^{1/2}
\]  

(1)
where $\Phi_p$ is the number of monomers per unit volume, $\alpha$ the statistical unit length of the polymeric chains, $\ell_B$ the Bjerrum length and $\kappa^{-1}$ the usual Debye-Hückel screening length defined in a salt-free solution by $\kappa^2 = 4\pi\ell_B \alpha \Phi_p$.

Also the model predicts that, for small enough $C_p$, the intensity at $q = 0$ varies as $I(0) \sim C_p/\alpha$ while the peak intensity scales roughly as $I(q^*) \sim C_p^{1/2}/\alpha$, which is again consistent with the observed increase of the relative peak intensity during dilution.

However quantitative agreement with theory is not achieved on this broad $C_p$ range. Figure 3 shows the variation of the measured peak position in terms of the variables in equation (1). This relation was found to be satisfactorily obeyed in the range $0.4 < C_p(M) < 1$ with $f = 0.05$ and $f = 0.10$ [4], which is observed here again for the samples within the same $C_p$ range (solid line). However, for the more dilute solutions clear deviations from equation (1) are visible. In particular straight lines through all data points corresponding to one given neutralization degree do not extrapolate to the origin and let us expect that the peak should disappear more rapidly with dilution than predicted.

![Figure 3](image)

Fig. 3. — Shift with polymer concentration of the peak position in the dilute solutions. Straight line is the theoretical prediction (Eq. (1) in the text).

In reference [4], it was shown that the theoretical structure factor derived within the random phase approximation (RPA) was able to describe well the experimental data in the range $0.57 < C_p(M) < 1$, $f = 0.05$. Three free parameters were allowed: the contrast factor $K$ between polymer and solvent, the statistical unit length $\alpha$ and an effective virial term $h(T, \Phi_p)$ depending only on temperature $T$ and polymer concentration $\Phi_p$. Quality of the fits was proved by the even distribution of the residues, the right order of magnitude for $K$ and $\alpha$ and the insensitivity of both parameters to variables like temperature, polymer or salt concentration. Again here, the fitting procedure works well for the two most concentrated solutions but the quality of the fits becomes much poorer for the largest dilutions: in addition to uneven distribution of the residues, $K$ and $\alpha$ parameters begin to drift and adopt more and more unphysical values.
This is not surprising since the general shape of the scattering curves is changing progressively with dilution. For the most dilute solution, the peak appears clearly narrower while the intensity at large $q$ values no longer follows a $q^{-2}$ power law but rather a slower decay with an apparent exponent about $-1.2$. As a consequence, the corresponding scattering curve does not coincide at large $q$ values with the other samples in figure 2. The same features are visible for the samples with the higher neutralization degree $f = 0.10$. They were observed as well with dilute poly(methacrylic acid) (PMA) solutions [19].

Some problems might be linked with the estimation of the real ionization degree at the dilution goes on [4]. However, although they might explain partly the drift in the $K$ and $a$ parameters values, they probably do not account for the change in the shape of the structure factor.

Thus the above observations show that the structure factor derived from RPA is no longer suited to describe our experimental data when $C_p < 0.5$ M. This is not completely unexpected since the mean field approximation should break down when correlations between chains become too strong. This limitation can be given a more precise meaning [20]. An isolated polyelectrolyte chain with $N$ monomers in a $\Theta$ solvent can be described as a strongly correlated alignment of Gaussian blobs [21]. Each thermal blob contains $N_b$ monomers, $N_b \sim (a/l_B)^{2/3} a^{-4/3}$, and the total end-to-end distance of the chain is [22]:

$$R \sim \left( \frac{N}{N_b} \right) a N_b^{1/2} \sim N a \left( \frac{l_B}{a} \right)^{1/3} a^{2/3}$$

Such chains in a semi-dilute solution will retain their extended conformation over a correlation length $\xi$ given by:

$$\xi \sim \left( \frac{l_B}{a} \right)^{1/3} a^{-1/3} (l_B \Phi_p)^{-1/2}$$

The latter expression is obtained by writing $\xi \sim R (\Phi_p/\Phi^*)^{-1}$ with $\Phi^* \sim N/R^3$ and requiring that powers of $N$ cancel to get the exponent $x = 1/2$ [23]. Strong correlations between the thermal blobs can be expected if $\xi$ is larger than their size, that is for concentrations smaller than

$$\Phi_p \sim \left( \frac{l_B}{a} \right)^{4/3} \frac{a^{2/3}}{a^2 l_B}$$

Beyond that concentration, the mean field approximation is probably satisfactory [20]. Qualitatively equation (4) predicts that departures from mean field behaviour upon dilution will occur sooner for higher ionization degrees. This is consistent with the data in figure 3 which are however too limited to check the exponent value. Also using the value $a = 8.9$ Å obtained from the straight line in figure 3, equation (4) gives a very good order of magnitude, e.g., $C_p \sim 0.3$ M when $\alpha = 0.05$, for the polymer concentration range above which mean field behaviour is expected.

It can be noticed that both the slower intensity decay at large $q$ values and the peak narrowing are consistent with the idea of long range order between extended chains. However in the present state these remarks are mere speculations. Clearly the elucidation of the structure of weak polyelectrolyte solutions in this concentration regime would need more theoretical effort, more extended data sets and more detailed polymer characterization. In this paper, the study of dilute solutions was only intended to provide us with references to be compared to swollen gels.
Gels in the reaction bath.

Figure 4 shows the effect of increasing cross-linking degree on the intensity scattered from gels in the reaction bath. The introduction of cross-links results in an increase in the scattering intensities with a larger effect at small $q$ values. This effect has already been observed in light scattering [6, 7] and SANS [7] experiments on this type of gels.

![Figure 4](image.png)

Fig. 4. — Scattering intensities of gels in the reaction bath with varying cross-linking degrees.

The total absolute coherent intensity scattered per unit volume of gel can be split as [24]:

$$I(q) = K_p^2 C_p^2 H_{pp}(q) + 2 K_p K_c C_p C_c^2 r_c H_{pc}(q) + K_c^2 C_p^2 r_c^2 H_{cc}(q)$$  \(5\)

where $H_{\alpha\beta}(q)$ is a partial structure factor relating to species $\alpha$ and $\beta$, $K_\alpha$ the contrast of species $\alpha$ with respect to the solvent and indices $p$ and $c$ stand respectively for monomer units and cross-linker units. In equation (5) the cross-linker concentration is written directly as $r_c C_p$. Equation (5) does not assume any particular model about the structure of the gel but simply recognizes that the total intensity is scattered from two types of scattering units.

The simplest way to analyze the excess of scattering intensity in the gels compared to a solution with the same concentration is to consider them as the superposition of two structures: a solution-like structure and a structure due to cross-links. The main underlying assumption in this approach is that the introduction of cross-links does not modify drastically the structure of the gels compared to an equivalent solution, i.e., cross-links act as a perturbation. This approximation is likely to remain valid as far as the gels are not close to their swelling equilibrium. For gels studies in the reaction bath, this means for small enough cross-linking degrees.

Even if this superposition principle is accepted to be true, one might consider that the fraction of polymer chains involved in the cross-linked structure reduces the polymer concentration in the solution-like structure. Therefore the definition of an equivalent solution to be compared to the gels might be rather difficult and a controversial subject. Geissler and coworkers [8-10] have tried to split the total intensity scattered from gels into two
contributions, taking into account an effective reduced polymer concentration in the solution-like structure. Such an effective reduced concentration is useful to interpret their repeated observations that swollen gels scatter less than solutions with same composition in the high $q$ regime. Our gels in the reaction bath do not exhibit that behaviour and scatter more than the solutions in the high $q$ range. This is not too surprising since in the sample preparation, the total amount of co-monomers is increasing with cross-linking degree, i.e., $C_{p,\text{tot}} = C_p (1 + r_c)$. Taking into account this feature and the fact that the gels are in their reaction bath, we adopt here the most natural choice and take the solution with the same monomer concentration and neutralization degree but no added cross-linker units as a reference sample to be compared to the gels. Thus we are assuming that the first term in r.h.s. of equation (5) remains simply the intensity scattered by the reference solution sample. We can then calculate the quantity $\Delta l (q) \equiv I_{\text{gel}} (q) - I_{\text{sol}} (q)$ and expect it to be the last two terms in equation (5). Figure 5 shows the resulting $\Delta l (q)$ normalized by the cross-linking degree as suggested by equation (5).

![Graph](image)

Fig. 5. — Excess scattering intensities of gels in the reaction bath with respect to the corresponding solution as a function of cross-linking degree. Curves are normalized by the concentration of cross-linking units. Straight line corresponds to a $q^{-4}$ decay.

A striking superposition of the results in the high $q$ regime can be noticed. This is also true, although with some scattering in the data points, for the sample with $r_c = 5 \times 10^{-3}$ which is not displayed in figure 5 for the sake of clarity. In this representation, the corresponding data points would distribute themselves around those belonging to the sample with $r_c = 0.01$.

This superposition could be tentatively understood simply in terms of the intensity scattered at high $q$ values being proportional to the total co-monomer concentration $C_{p,\text{tot}}$. However normalizing the scattering curves in figure 4 by $C_{p,\text{tot}}$ does not help so much in reducing their different level at high $q$ values. This is simply because cross-linker and monomer units are discernable in the SANS experiments: in fact, numerical estimates for the contrast factors show that $K_c$ is larger than $K_p$ by a factor about 2 [25]. Thus the total scattering intensity cannot be thought of as simply due to the arrangement of monomer units with the cross-linker units being neglected or included in an effective total concentration.
It can be noticed the superposition in itself is no regular proof that the solution-like structure of the gel in the reaction bath is not affected by the presence of cross-linking points, i.e., that we are entitled to identify the first term in equation (5) with \( I_{\text{sol}}(q) \). The proportionality to \( r_c \) is not necessarily linked to an intensity scattered from cross-linker units alone and the evolution of scattering intensities with increasing \( r_c \) might be due to intricate changes in the three terms of equation (5). However we believe our assumption is not too bold for gels in the reaction bath when the cross-linking degree is small enough. Its exact range of validity should be checked by the contrast variation method.

Free radical copolymerization of acrylamide and bisacrylamide is known to yield heterogeneous gels due to the different reactivity ratios of the two co-monomers and to the poorer solubility of bisacrylamide in water [9, 26]. This is likely to remain true when acrylic acid is used instead of acrylamide. This mechanism could explain the evolution of the spectra displayed in figure 4 that would be due to the formation of regions richer in cross-linking units. The sharp decrease of \( \Delta I(q) \) at large \( q \) values in figure 5, \( \Delta I(q) \sim q^{-4} \), \( x = 4 \), together with the assignment of \( \Delta I(q) \) to the last two terms in equation (5), would then suggest that these regions have relatively well-defined interfaces. It would be tempting to use a standard analysis [27] of these results to obtain the volume fraction and the specific surface area of the dense regions. Such an analysis is here subject to uncontrolled errors since our \( \Delta I(q) \) includes a cross-correlation term \( H_{pe}(q) \) with unknown magnitude. Here again the contrast variation method should be useful to obtain more quantitative information.

The SANS intensity at the smallest \( q \) value (\( q = 9.67 \times 10^{-3} \) \( \text{Å}^{-1} \)) can be compared to the light scattering intensity measured on similar samples in \( \text{H}_2\text{O} \) (\( q = 2.42 \times 10^{-3} \) \( \text{Å}^{-1} \)) [16]. Figure 6 shows the evolution of these values as a function of cross-linking degree. For convenience, intensities are normalized to obtain \( I_q(r_c = 0) = 1 \) with both techniques. In the SANS experiments, extrapolated values with reasonable error bars have been used in the few cases where the first detector cell gives aberrant values. The evolution of the two data sets is qualitatively the same. However no quantitative comparison is possible because of the differences in the explored \( q \) range, in the contrast factors and in the solvent quality.

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Fig. 6. — Evolution with cross-linking degree of light and neutron scattering intensities at fixed \( q \) value: light scattering (LS), \( q = 2.42 \times 10^{-3} \) \( \text{Å}^{-1} \), neutron scattering (SANS), \( q = 9.67 \times 10^{-3} \) \( \text{Å}^{-1} \). LS data are from reference [16].
Swollen gels.

In contrast with gels in the reaction bath, the preparation of swollen gels with a given swelling ratio involves many steps which are liable to introduce errors. Therefore several samples with the same $C_p$ and $f$ values were studied to test reproducibility which was found overall very satisfactory. Figure 7 shows some typical examples for gel samples with $f = 0.10$.

![Figure 7](image)

Fig. 7. — Typical examples for reproducibility in the scattering intensities of swollen gels. Here for $Q = 1.05$, 1.95 and 4.63 ($f = 0.10$).

The main new feature observed on the swollen gels is the presence of an upturn in the intensity at low $q$ values. In the previous section, such effect was observed only for gels with $r_c$ larger than 0.03. This difference is ascribed to the presence of charges during the synthesis for the latter gels but this point will be discussed later in the next section. The strong increase of the intensity at low $q$ values makes the determination of a peak position very difficult in the swollen gels especially at large polymer concentrations ($f = 0.10$). When the neutralization degree is only 0.05, the peak becomes merely a shoulder at all concentrations. The shift of this shoulder seems correlated with the shift of the peak in the corresponding solutions (Fig. 8).

A striking feature in figure 8 is the difference between the intensities scattered from the gels and from the solutions in the high $q$ regime. This effect is observed for all gels. Moreover that difference appears to be, in the large $q$ regime, independent of $q$ and constant, within the experimental accuracy, whatever the polymer concentration and the ionization degree. This is shown in figure 9 where $\Delta I(q) = I_{gel}(q) - I_{sol}(q)$ is plotted for a few samples. The same observations were made during previous unpublished experiments and the fear of possible artifacts was the reason for a new set of experiments including the study of solutions and gels with varying $r_c$.

An obvious explanation for this unusual behaviour would be incorrect subtraction of the incoherent scattering. For this set of samples, the use of monomer solutions without cross-linker units as background samples could be a priori incriminated. However incoherent scattering was measured as a function of $r_c$ and found to increase by 10% when $r_c$ varies from 0 to 0.05 and polymer concentration is 1.1 M. Here $r_c = 0.01$ so that the error on
the incoherent scattering level would be only 2% for gels in the reaction bath but would become much smaller for the swollen gels. In fact polymer contribution is less than 12% of the total incoherent scattering at $Q = 8$ where $D_2O$ is the main source of incoherent scattering. Therefore the difference between gels and solutions would decrease with the polymer concentration and be anyway smaller than the observed one.

This difference between gels and solutions with the same concentration could again raise the question whether these solutions are correct reference samples for the gels. Before going to that point we want first to examine more carefully the treatment of the data.

An important quantity that is measured during the SANS experiments and relevant for the treatment is the transmission of the samples. In our experiments, transmission values were measured with low counting rates and large number of total counts to reduce the relative
statistical error on the final transmission values to about 0.3%. Interestingly, transmission values for the solutions and the gels in the reaction bath are equal within this statistical error to that of their corresponding background samples. Meanwhile transmission values in the swollen gels are systematically 5 to 8% smaller than in the background samples. This fact was also noticed in the first set of experiments.

Our tentative interpretation for this result is a possible contamination of the samples by atmospheric H₂O during the swelling process. The possibility for such a contamination was also found recently in an other experiment on a stretched PAA gel swollen in D₂O [28]. This phenomenon would imply that the incoherent scattering in the swollen gels is underestimated if it is taken from the monomer solution in pure D₂O. To account for this effect we performed a different treatment of the data by taking as background samples equivalent monomer solutions with same transmission as the gels. The level of incoherent scattering for these equivalent background samples was calculated by interpolation through the data in figure 1. For samples with 6 mm thickness, the transmission for a 5 mm thickness was estimated as:

\[
\text{Tr}(5 \text{ mm}) = \text{Tr}(\text{EC}) \left( \frac{\text{Tr}(6 \text{ mm})}{\text{Tr}(\text{EC})} \right)^{5/6}
\]

where Tr(EC) stands for the transmission of the empty cell. Equation (6) expresses simply Beer-Lambert's law, the validity of which was checked previously for this range of transmission values and sample thicknesses [29].

Figure 10 shows the corrected spectra for the same samples as in figure 8. It can be seen that the difference between gels and solutions at large q values has vanished with the more elaborate treatment taking into account a possible contamination by protonated water. The calculated change in incoherent scattering level would correspond to a content of about 0.02 mole of protonated water per mole of solvent. This rather large value could be explained by the procedure used to swell the gels. Contamination by atmospheric water would probably be no problem if the gels were swollen in an excess of D₂O. The latter procedure is however not very convenient to achieve swelling ratios smaller than the swelling equilibrium.
Fig. 10. — Same as figure 8 but incoherent scattering level in the swollen gels has been adjusted to match their transmission values (see text).

It can be noticed that errors in polymer concentration could also explain the differences seen in figure 8. After the scattering experiments, the masses of the dried gels were compared to those of the swollen gels. Swelling ratios estimated by that method agree within a few percent with the values given in table I, provided residual water due to incomplete drying is taken into account. This amounts to about 0.07 wt/wt (resp. 0.11 wt/wt) for gels with $f = 0.05$ (resp. $f = 0.10$). Thus no important error in the concentration was made. Moreover, in view of the systematical deviation depicted in figure 9, we believe our hypothesis of $H_2O$ contamination is the most likely.

Anyway, if we consider that the transmission values of the samples are linked to their incoherent scattering level, a statement sustained by identical transmission values for dilute
solutions or gels in the reaction bath and their corresponding background samples, then the correct treatment for the swollen gels data is the second one, whatever the reason for the anomaly in their transmission values.

It is worth noticing that equations for the subtraction of incoherent scattering have been proposed to take into account different transmission values for samples and background samples [10a]. In the present case these equations yield erroneous results since the intensity scattered from a solution sample (S2f10) is found to be larger by about 20 % when corrected with a more dilute background sample (B5f10) than when corrected by using the appropriate background sample (B2f10). In a similar way, the corrected intensity is smaller by about 20 % when incoherent scattering is subtracted by using a more concentrated background sample (B1f10). These variations might be due to multiple incoherent scattering effects and point out the necessity in some cases to spend more time on counting background samples with composition close to that of the samples.

Figure 11 shows the variation with polymer concentration of the intensity scattered at \( q = 9.67 \times 10^{-3} \text{ Å}^{-1} \) from gels and solutions. Extrapolated values were used as necessary like in figure 6 (see above). It can be seen that the intensities scattered from the solutions is within a good approximation proportional to the polymer concentration, i.e., the extrapolation to \( C_p = 0 \) is close to zero. On the other hand, the intensities scattered from the gels decrease with slopes slightly larger than in the corresponding solutions but an extrapolation from the same polymer concentration range does not go to the origin. A similar behaviour was noted in light scattering experiments at smaller \( q \) values [16].

![Graph](image_url)

**Fig. 11.** — Evolution with polymer concentration of the scattering intensity at fixed \( q \) value (\( q = 9.67 \times 10^{-3} \text{ Å}^{-1} \)) for dilute solutions (closed symbols) and swollen gels (opened symbols).

**Synthesis procedure and gel structure.**

In figure 12 are grouped the spectra measured for gels and solutions with \( f = 0.10 \) and polymer concentration equal or close to the concentration of preparation. Samples labelled as being in the reaction bath (solid symbols) are taken from figure 4 and have been made directly in the
Fig. 12. — Influence of the synthesis procedure on the intensity scattered from gels and solutions with concentrations close to the one in the reaction bath. Slight differences in concentrations (≤ 5 %) are taken into account through the factor $Q$. Closed symbols : neutralization before the polymerization ; opened symbols : neutralization after the polymerization.

scattering cell, the neutralization being performed prior to the polymerization reaction. Data labelled by opened symbols corresponds to samples synthesized in the absence of charges and subsequently neutralized by adding a small amount of concentrated NaOH solution. The intensities scattered from these gels have been treated with the refined procedure accounting for their lower transmission values. The small differences in polymer concentration are taken into account by normalizing the scattering intensities with the corresponding $Q$ values (Tab. I). In the large $q$ region, all the samples display the same behaviour within the experimental accuracy.

Solution samples prepared by the two different paths show very similar scattering curves as expected. For these samples, the presence of charges is thought to modify only the reaction rate constants and thus to affect slightly the distribution of molecular weights of the linear chains. Such effects cannot be distinguished in a concentrated solution.

Gel samples on the other hand exhibit large differences in the small $q$ region where the gels synthesized without charges show a strong increase in the scattering intensity.

Summary and discussion.

In the reaction bath the introduction of cross-linking points results in an additional contribution to the scattering intensity. The total scattering intensity has to be interpreted in terms of a two-component system due to the different contrasts of monomer and cross-linker units with respect to the solvent. If the solution sample is used as a reference the extra scattering can be
normalized by bisacrylamide content and decreases sharply for large \( q \) values. These results support the picture of inhomogeneous distribution of cross-linkers in the gels. This inhomogeneity could be explained by the different reactivity ratios of the two co-monomers and by the poorer solubility of bisacrylamide in water [26].

Except for the higher cross-linking degrees, the peak position is not affected very much by the presence of cross-links. This is consistent with previous experiments that have shown a larger effect when the neutralization degree decreases [7]. Here, since \( f = 0.10 \), electrostatic interactions have still a dominant role to impose a length scale in the fluctuations of polymer concentration.

If charges are added to the gels only after the polymerization reaction is completed, the excess of scattering intensity at small \( q \) increases for a given \( r_c \) value. This could suggest that poorer solvent conditions in the reaction bath help to create more inhomogeneous regions that are expected to include to some extent linear chain portions. However it must be kept in mind that the presence of charges during the synthesis could also yield different topologies and defects for the gels. Shear modulus measurements could be helpful to resolve this point and are under way.

In the course of dilution, the peak shifts to smaller \( q \) values in the solution samples. As soon as the polymer concentration is smaller than 0.5 M, this shift is no longer described by equation (1), contrary to what was observed in previous experiments at higher concentrations [4]. Also the general shape of the structure factor can no longer be calculated by the random phase approximation.

In the gels, swelling induces a similar shift of the maximum. However the exact position of the peak is difficult to locate due to the upturn in the intensity at small \( q \) values. In the gels with \( f = 0.05 \), the situation is even worse since only a shoulder can be distinguished in the spectra.

Within our experimental accuracy, it is not possible to decide unambiguously whether the intensity scattered from the swollen gels at high \( q \) values is larger, equal or smaller than in the corresponding solutions. Geissler and coworkers [8-10] have reported smaller intensities in the gels while Bastide and coworkers [11-13] found good agreement between gels and solutions with same concentration. Here, depending on the samples, we find small positive or negative values for \( \Delta I(q) \) that would favour same large \( q \) intensities for gels and solutions and correspond to the intuitive result that the intensity at large \( q \) values remains proportional to the average concentration in scattering units, provided no changes occur in statistical unit length or chain conformation.

The swelling is associated to a decrease of the small \( q \) intensity for both gels and solutions. The observed behaviour parallels previous observations in light scattering experiments [16]. The latter have shown the presence of frozen fluctuations of polymer concentration in the gels, i.e., with a characteristic decay rate generally much smaller than that of the thermal fluctuations in polymer concentration that are associated to the cooperative diffusion coefficient in gels and solutions. These frozen fluctuations contribute for a large part of the intensity scattered from the gels. In fact it was shown that all the excess of scattering intensity in the gels with respect to the solutions could be attributed within experimental error to these frozen fluctuations. Upon swelling this contribution was shown to remain approximately constant while the contribution arising from thermal concentration fluctuations was decreasing. This result is qualitatively recovered in the SANS experiments (Fig. 11). It can be noticed that these experiments are equivalent to light scattering experiments in which detection is performed on a large number of coherence areas and the frozen fluctuations contribute only through an ensemble-averaged mean value.

However we want to emphasize that samples studied with the two techniques were different. In the SANS experiments swollen gels were synthesized in D\(_2\)O prior to the neutralization
while in the light scattering experiments polymerization took place in H₂O after the neutralization. Thus the structure factor for the latter samples was probably closer to the ones plotted in figure 4 since the intensity was found independent of \( q \) in the light scattering \( q \) range [16]. Here the situation is quite different since no reasonable extrapolation to \( q = 0 \) can be obtained from the curves in figure 10. Therefore no quantitative meaning can be given to the decay of \( I_q \) with the swelling degree in the present gels.

The small \( q \) excess of scattering intensity in the gels compared to the solutions with same concentration is usually interpreted in terms of heterogeneities in polymer concentration [8-12, 14]: in gels prepared at a given concentration, the fluctuations in cross-linking density, which are inherent to a random process, show up upon swelling because regions with varying cross-linking density swell differently, thus giving rise to frozen fluctuations of polymer concentration in the gel [14]. On the other hand, in a solution, chains disentangle upon dilution, the fluctuations in polymer concentration equilibrate and are given by the osmotic compressibility in the solution [23]. Thus differences between gels and solutions are expected to grow up as the concentration decreases from the concentration in the reaction bath to the swelling equilibrium concentration. The above picture is consistent with our results with some differences compared to the case of neutral gels.

The small \( q \) intensity decreases in charged systems upon dilution or swelling while it is the reverse in neutral systems [23]. This is simply due to the dominant contribution of the electrostatic energy in the osmotic pressure for the former systems [21, 30].

More important is the small influence of swelling degree on the excess of scattering intensity in our gels while in neutral gels a large increase is usually observed when the concentration decreases [8-12]. The latter phenomenon can be explained if the densely cross-linked regions are considered to have a branched structure and a size distribution analogous to the ones obtained in a percolation model or, more generally, if the swelling is associated to the disinterpenetration of more or less branched dense regions that are overlapping [14].

In our experiments, the small sensitivity of the frozen contribution to the swelling and the sharp decrease of that contribution at large \( q \) values (Fig. 5) do not agree with the above picture. Our results seem to suggest a more compact structure for dense regions, which could be explained by chemistry. A more precise picture is however difficult to extract from the present experiments. The change of the gel structure according to the step where neutralization is performed indicate that the thermodynamic state of the gelling system plays a decisive role to tune the size and amplitude of the frozen fluctuations of concentration. That effect has been observed as well in neutral gels [31, 32]. The situation is here more complex since in the reaction bath there is a coupling between the chemistry, the solvent quality and the length scale of thermal fluctuations in polymer concentration that is fixed by the screening of the electrostatic interactions. The showing up of the resulting structure upon swelling is coupled as well to that last parameter.

To conclude, returning to the question raised in the introduction, we would say that these PAA gels exhibit frozen fluctuations of polymer concentration that seem more compact than the ones usually observed so far in neutral gels. The extent and the amplitude of these frozen fluctuations can be reduced noticeably by performing the neutralization before the synthesis.

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