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A. Moussaid, J. Munch, F. Schosseler, S. Candau. Light scattering study of partially ionized poly(acrylic acid) systems: comparison between gels and solutions. *Journal de Physique II*, 1991, 1 (6), pp.637-650. 10.1051/jp2:1991195 . jpa-00247546

HAL Id: jpa-00247546

<https://hal.science/jpa-00247546>

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Classification

Physics Abstracts

61 25H — 82 70 — 05 90

Light scattering study of partially ionized poly(acrylic acid) systems : comparison between gels and solutions

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(Received 19 November 1990, accepted 6 March 1991)

Résumé. — Des mesures de diffusion statique et quasiélastique de la lumière ont été effectuées sur des solutions et des gels d'acide poly(acrylique) partiellement ionisés. L'intensité diffusée par les gels est indépendante du vecteur d'onde de transfert, ce qui montre leur homogénéité, contrairement au cas des gels neutres. La comparaison des moyennes temporelle et spatiale de la fonction d'autocorrélation de l'intensité de la lumière diffusée montre que ces gels se comportent comme des milieux ergodiques. Les variations de l'intensité diffusée par les gels et les solutions en fonction de la concentration en polymère et du degré d'ionisation sont en bon accord avec les prédictions théoriques. Les variations du coefficient de diffusion avec ces mêmes paramètres sont identiques pour les gels et les solutions.

Abstract. — Static and quasielastic light scattering experiments have been performed on the reaction bath of partially neutralized poly(acrylic acid) solutions and gels. The intensity scattered from gels is independent on the scattering wavevector, giving thus evidence that the gels are homogeneous at the scale of the wavelength of the light, contrary to what is generally observed in neutral gels. The comparison of the time and ensemble averages of the autocorrelation function of scattered light intensity shows that the gels behave with respect to that experiment as ergodic media. The variations of the intensity scattered from gels and solutions, with the ionization degree and the polymer concentration were found to be in good agreement with those predicted from simple theoretical arguments. The variations of the cooperative diffusion with these same parameters were found similar for gels and solutions.

Introduction.

Static and dynamic light scattering experiments have revealed a complex picture of the properties of polyelectrolyte solutions in the absence of low molecular weight salt [1]. An unexpected result of dynamic light scattering (DLS) experiments is the existence of two diffusive modes in semi-dilute solutions, a fast one attributed to a cooperative diffusion and a slow one whose origin is not yet understood but which is believed to be associated with the

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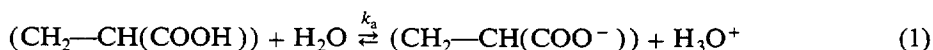
diffusion of clusters of molecules [2]. This behavior was observed in various polyelectrolyte systems regardless of their local chemical structure (e.g. bovine serum albumin [3], polynucleosomes [3], sodium polystyrene sulphonate [4], poly(methacrylic acid) [5]). It was shown recently that, contrary to the case of semi-dilute solutions, there is no slow mode in the spectrum of the light scattered by swollen crosslinked networks of partially neutralized poly(acrylic acid) (PAA) [6-9]. Static light scattering experiments (SLS) performed on the same systems showed that the scattered intensity is dominated by the effect of the electrostatic interactions, in good agreement with the theoretical predictions for semidilute solutions of polyelectrolytes. The structure factor obtained from small angle neutron scattering (SANS) was found to exhibit a peak in limited ranges of ionization degree and polymer concentration [8, 9]. The variations of the amplitude and of the position of the peak as a function of the ionization degree are reasonably described by a recent theoretical model developed for semi-dilute solutions of weakly charged polymers in a poor solvent [10, 11]. The ensemble of the results obtained in the study quoted above show that, with the notable exception of the absence of a slow mode in the spectrum of scattered light, gels exhibit a behavior very similar to the one expected for semi-dilute solutions.

Usually gels reveal the presence of submicroscopic inhomogeneities associated with non random crosslinking [12-15]. Moreover it was argued recently that crosslinking might invalidate the ergodic hypothesis i.e. introduce a difference between the time and ensemble averages of the autocorrelation function of scattered light intensity. In this paper we are interested in these two characteristic features that are associated with the presence of crosslinks. We compare, in the reaction bath, swollen crosslinked networks and the corresponding semi-dilute solutions of partially neutralized PAA. From the dynamic light scattering (DLS) experiments, we are able to compare the shape of the autocorrelation function for both gels and solutions and to study the variations of the cooperative diffusion constant as a function of polymer concentration and ionization degree.

1. Materials and methods.

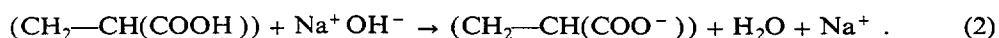
1.1 SAMPLE PREPARATION. — The solutions of poly(acrylic acid) are prepared by radical polymerization of acrylic acid in aqueous solution. Gels are obtained by radical copolymerization of acrylic acid and methylene bisacrylamide. Both reactions are initiated by ammonium peroxydisulfate.

The degree of ionization α of the PAA is defined as the ratio of carboxylate groups to the total number of monomers. PAA is a weak acid, the ionization degree can be varied over a very wide range, by changing the pH of the medium. In aqueous solution, α has a non zero value due to the acidobasic equilibrium:



At the concentrations used in this study, $2 \times 10^{-2} \text{ g cm}^{-3}$ (0.278 M) — $15 \times 10^{-2} \text{ g cm}^{-3}$ (2.08 M), the dissociation of the polyacid is very low. Thus, we have approximated the dissociation constant to that of the monomeric acrylic acid: $k_a = 5.6 \times 10^{-5}$. This leads to values of α decreasing from 1.1×10^{-2} to 5×10^{-3} when the polymer concentration increases from 0.278 M to 2.08 M.

High ionization degrees ($\alpha > 10^{-2}$) are obtained by addition of NaOH to the solution in order to partially neutralize the polyacid to a given stoichiometric ionization degree according to



This leads to an ionic strength $I \equiv \alpha$, due to the counterions Na^+

Very low ionization degrees ($\alpha < 5 \times 10^{-3}$) were obtained by addition of HCl to the solution to shift the dissociation equilibrium of the weak acid towards the acidic form.



A standard procedure is used to prepare the samples. The acrylic acid and ammonium peroxydisulfate — with methylene bisacrylamide if we want to obtain a gel — are added to a solution of water containing the amount of sodium hydroxide or HCl to get a given ionization degree. The solution is filtered with a $0.2 \mu\text{m}$ filter to get rid of dust particles. A few cm^3 are then poured in a light scattering cell. Nitrogen is bubbled in the solution to remove the dissolved oxygen which would inhibit the radical reaction. The reaction is carried out in an oven at 70°C during 6 h. Classical light scattering experiments performed in dilute brine solutions (0.1 M NaBr) showed that the weight average molecular weight M_w of the polymer chains decreases from $M_w = 1.1 \times 10^6$ to $M_w = 6.5 \times 10^5$ when the ionization degree in the reaction bath (polymer concentration $C_p = 0.707 \text{ M}$) increases from $\alpha = 8.9 \times 10^{-3}$ to $\alpha = 0.3$.

1.2 LIGHT SCATTERING EXPERIMENTS. — DLS experiments provide the normalized time intensity correlation function (ICF) $g^{(2)}(q, \tau)$ of the scattered intensity defined as

$$g^{(2)}(q, \tau) = \frac{\langle I(q, 0) I(q, \tau) \rangle}{\langle I(q, 0) \rangle^2} \quad (4)$$

where $I(q, \tau)$ is the scattered intensity at time τ and scattering vector q , $q = (4\pi n/\lambda) \sin \theta/2$, λ , θ and n being the wavelength of the light, the scattering angle in the vacuum and the refractive index of the medium, respectively. The angular brackets stand for an ensemble average but in practice the correlator provides data with the ensemble average replaced with a time average. This procedure is justified for ergodic media. Moreover, for scattering processes in which the scattered field is a zero-mean complex Gaussian variable $g^{(2)}(q, \tau)$ can be written:

$$g^{(2)}(q, \tau) = 1 + \beta |f(q, \tau)|^2 \quad (5)$$

where $f(q, \tau)$ is the normalized intermediate scattering function and $\beta (\leq 1)$ is the coherence factor that depends on the experimental geometry. In the light scattering set-up used in this study, the optical source is a Spectra Physics argon ion laser operating at 4880 \AA . The time-dependent correlation function of the scattered intensity is derived by using a 64 channel digital correlator (Brookhaven B1 2030). Experiments performed on model latex suspensions give $\beta \approx 0.9$. The scattering angle is varied between 20° and 150° . A device using a step by step motor allows us to rotate and translate the scattering cell so that various scattering volumes into the sample can be probed. Such a device allows one to estimate the normalized ensemble-averaged ICF $g_E^{(2)}(q, \tau)$ by combining time-averaged intensities and unnormalized ICF measured for a series $p = 1$ to P of different scattering volumes

$$g_E^{(2)}(q, \tau) = \frac{\langle \langle I_p(q, 0) I_p(q, \tau) \rangle_T \rangle_E}{\langle \langle I_p(q) \rangle_T \rangle_E^2} \quad (6)$$

where the symbol $\langle \rangle_E$ stands for an ensemble averaging. For ergodic media the above procedure leads to same results as time averaging.

Intensity correlation data are routinely processed by using the method of cumulants [17, 18] to provide the average decay rate $\langle \Gamma \rangle$ and the variance

$$v = (\langle \Gamma^2 \rangle - \langle \Gamma \rangle^2) / \langle \Gamma \rangle^2 \quad (7)$$

The cooperative diffusion coefficient D_c is related to the time constant τ_c ($\langle \Gamma \rangle = \tau_c^{-1}$) of the time correlation exponential decay through

$$D_c = (2 q^2 \tau_c)^{-1}. \quad (8)$$

Most experiments were performed at $T = 25^\circ \text{C}$.

2. Submicroscopic structure of the gels.

Static light scattering and SANS experiments performed on swollen crosslinked networks of neutral chains, have revealed the presence in the low q range of an excess of intensity that was attributed to quasistatic swelling inhomogeneities [12-15]. This extra scattering depends significantly on both the method of synthesis of the gels and the swelling degree. It is always large in gels swollen at saturation in a good solvent whatever the method of preparation [12-15]. An excess of scattering is also observed in the reaction bath for gels prepared *via* radical or anionic processes [15]. On the other hand when the gels are synthesized by means of methods liable to produce random arrangement of crosslinks, the scattered intensity from the gel in the reaction bath is very close to that of a semi-dilute solution [15].

Figure 1 shows the variations of the scattered intensity as a function of q^2 for PAA gels at polymer concentration $C_p = 0.707 \text{ M}$ and three different ionization degrees: $\alpha \sim 0$, 8.9×10^{-3} , 0.1 . It is seen that the scattered intensity decreases strongly as the ionization degree is increased. One observes also that the scattering intensity is a decreasing function of q for neutral gels but becomes q independent for ionized gels. This suggests that the presence of electrical charges in the network chains suppresses the concentration inhomogeneities. It must be noted that this effect is observed regardless the neutralization takes place prior or after the gelation process. The above results can be interpreted on the basis of the model developed by Borue — Erukhimovich [10] and Joanny — Leibler [11] for semidilute solutions of weakly charged polyions having an amphiphilic character due to a poor solubility of the polymer backbone in water. According to this model, these systems are liable to form mesophases consisting in polymer dense and polymer dilute regions arranged in a periodic array. Above the mesophase separation transition, the structure factor $I(q)$ has a peak at a finite wave vector q^* that fixes the period of the mesophase. Such a peak was indeed observed in the SANS spectra obtained for the PAA gels. The wavevector q^* is of the order of 10^{-2} - 10^{-1} \AA^{-1} , i.e. much larger than the scattering wavevector in light scattering experiments. Therefore it can be assumed that the presence of electrical charges produces a rearrangement of the chains to give rise to fluctuations with a characteristic length of the order $2\pi/q^*$ so that the gels appear homogeneous at the scales probed by light scattering. If the above picture is correct, one would expect the scattered intensity from the gel to be close to that scattered from a semi-dilute solution at same polymer concentration and ionization degree. The excess of intensity scattered from a solution of polyelectrolytes with respect to the solvent is given by [7, 8, 10, 11, 19]:

$$\Delta I_{\text{sol}} \sim C_p^2 / (K_{\text{os}} + K_{\text{os},e}) \quad (9)$$

where K_{os} and $K_{\text{os},e}$ are the contributions of respectively the neutral polymer chains and the free counterions to the osmotic compressional modulus. The dominant contribution comes

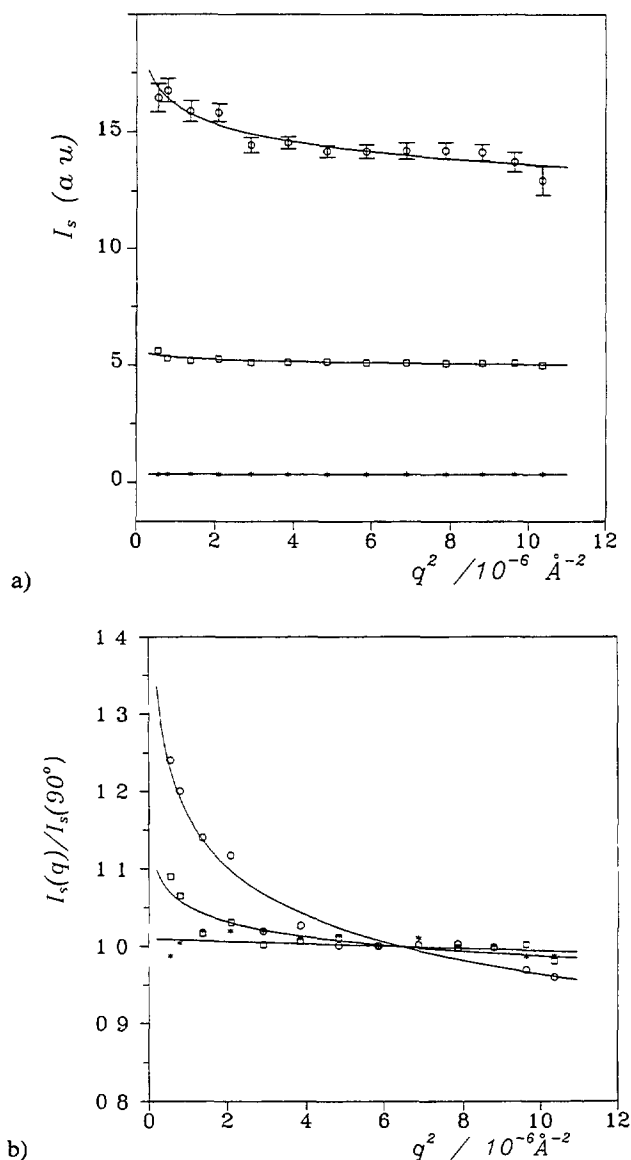


Fig 1 — a) Scattered intensity *versus* scattering wavevector for gels at concentration $C_p = 0.707 \text{ M}$ and different ionization degrees (O) $\alpha \sim 0$ (pH = 1), (\square) $\alpha = 8.9 \times 10^{-3}$, (*) $\alpha = 0.1$ b) Scattered intensities normalized by the intensity scattered at 90° for the same samples

from $K_{os, e} \sim k_B T C_p \alpha$ as soon as the ionization degree is larger than a few per cent [7, 8]. For gels equation (9) should also apply if one replaces K_{os} by $M_{os} = K_{os} + 4/3 \mu$ where M_{os} and μ are respectively the longitudinal and shear modulus.

Figure 2 shows the variation of I_{sol}/I_{gel} as a function of the ionization degree for a polymer concentration $C_p = 0.707 \text{ M}$. It is seen that this ratio is of ~ 0.7 for a quasi neutral system and tends towards a value close to 1 as α is increased. The excess of intensity scattered from the gel with respect to that of the solution, in the range $\alpha \sim 0$ can be attributed totally or in part to the effect of the inhomogeneities since for this system the scattered intensity decreases as q

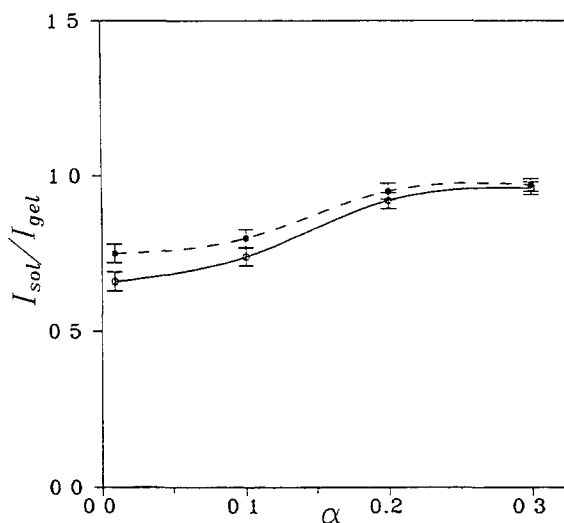


Fig. 2 — Variations of the ratio of the intensity scattered by a solution over that scattered by the gel for a polymer concentration $C_p = 0.707$ M as a function of α (O) $T = 25$ °C, (●) $T = 15$ °C

increases (cf Fig 1). It is also observed that at lower temperature the ratio $I_{\text{sol}}/I_{\text{gel}}$ is close to unity in the whole α range investigated. At low temperature, as it will be shown in a forthcoming paper, the scattered light comes predominantly from critical fluctuations that mask the contribution from the inhomogeneities.

On the other hand, the effects of inhomogeneities are not likely to explain the results obtained in the intermediate α range, i.e. $\alpha \sim 0.1$, since for these systems the scattered intensity is found q independent. One cannot invoke either an effect of the shear modulus since it would give a scattered intensity larger for the solution than for the gel. No explanation can be given at the moment for this small effect. The comparison between gels and solutions is

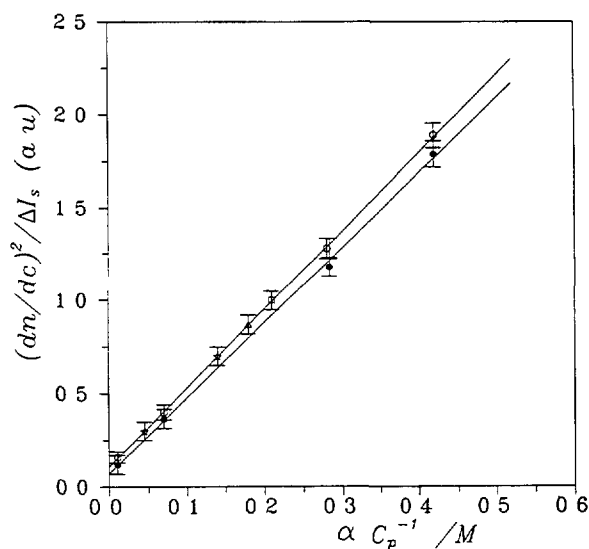


Fig. 3 — Variations of the inverse excess of scattered intensity with α/C_p for gels (full symbols) and solutions (open symbols). $C_p = 0.555$ M (Δ), 0.707 M (O, ●), 1.4 M (\square), 2.2 M (*)

also illustrated by figure 3 that shows the variations of the inverse excess of scattered intensity ΔI_s , corrected for the variation of the refractive index increment (dn/dc) with α [8], as a function of α/C_p for both gels and solutions. Within the experimental accuracy, the data are fitted by two straight lines slightly shifted. The positive intercepts correspond to the contributions of the neutral systems. Strictly speaking, the intercept should be dependent on the polymer concentration but the experimental accuracy doesn't allow to detect this effect.

3. Effects of the restricted motion of the scatterers in dynamic light scattering experiments.

3.1 ERGODICITY OF THE AUTOCORRELATION FUNCTION OF THE SCATTERED LIGHT. — Due to the presence of permanent crosslinks, the polymeric elements of a swollen network are localized near fixed average positions and are able only to execute limited Brownian motions about these positions. In the course of a single experiment, the system might not explore enough of the phase space that the time average inherent in the measurement of a property gives a good estimate of the ensemble average. With respect to that experiment the medium is non ergodic. The effect of non ergodicity on DLS has been theoretically studied by Pusey and Van Megen [16].

These authors state that the total scattered field $E_p(q, t)$ from a single scattering volume, that is for a given sub-ensemble p of a non ergodic medium, is not a zero-mean complex Gaussian variable but can be written as the sum of a fluctuating component E_{pf} that is a zero-mean complex Gaussian variable and a time-independent component E_{pc}

$$E_p(\mathbf{q}, t) = E_{pf}(\mathbf{q}, t) + E_{pc}(\mathbf{q}). \quad (10)$$

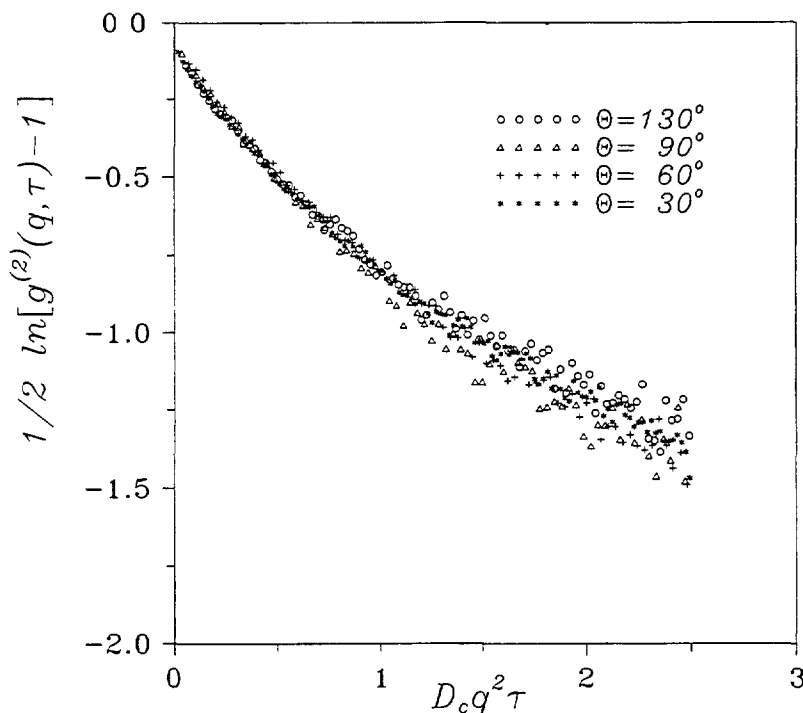


Fig. 4 — Semi-logarithmic plot of the square root of the normalized time averaged ICF obtained for a gel with $C_p = 0.707$ M and $\alpha = 8.9 \times 10^{-3}$ at four different scattering angles

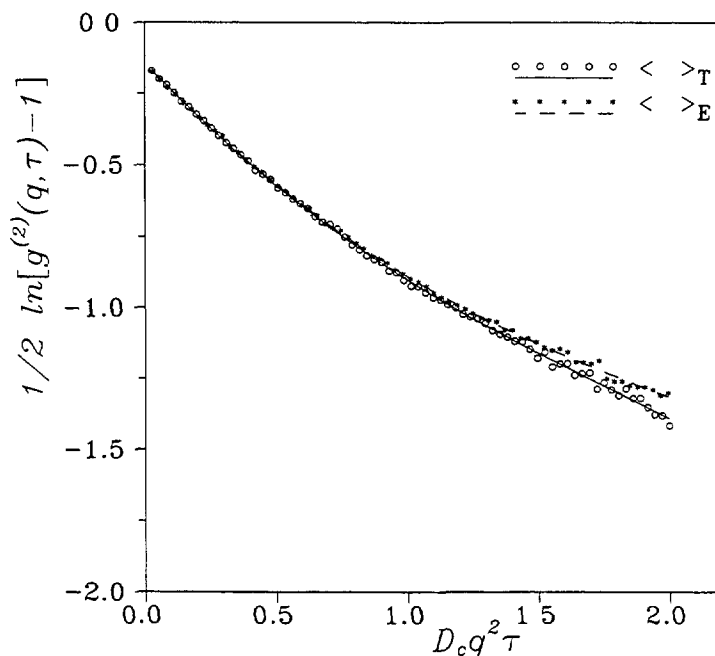


Fig 5 — Comparison between normalized time averaged ($\langle \rangle_T$) and ensemble averaged ($\langle \rangle_E$) ICF obtained for a gel with $C_p = 0.707$ M and $\alpha = 8.9 \times 10^{-3}$.

When sampled over the whole ensemble, the constant component $E_{pc}(q)$ is a zero-mean complex variable so that the corresponding intensity $I_{pc}(q)$ is distributed exponentially and can, depending on the set of average positions of the scatterers, take any value between 0 and ∞ . In a light scattering experiment on a single scattering volume, the time averaged intensity $\langle I_p(q) \rangle_T$ is easily obtained. If the system behaves as non-ergodic medium, this average intensity depends on the scattering volume considered and one should observe a negative exponential distribution of the recorded intensity as the sample is scanned through the laser beam so that many independent scattering volumes are illuminated.

We have performed such experiments for the PAA gels investigated here. We found that for all systems with ionization degree $\alpha \geq 8.9 \times 10^{-3}$, the time averaged intensity scattered from many different locations within the sample (scattering volume $\sim (200 \mu\text{m})^3$) and at different scattering angles was constant within 5%. Only the sample at ionization degree $\alpha \sim 0$ showed rather large fluctuations of the scattered intensity [$\pm 50\%$] at low q ($q \sim 0.89 \times 10^{-3} \text{ \AA}^{-1}$).

Another test of the ergodic behavior of a system is given by the comparison between the time averaged ICF $g_T^{(2)}(q, \tau)$ obtained on a single scattering volume and the ensemble averaged ICF $g_E^{(2)}(q, \tau)$ (cf. Eq. (6)). The latter is obtained by measuring unnormalized time-averaged ICF for many different scattering volumes within the sample, summing these functions and then normalizing by the square of the summed intensities. Figure 4 shows typical results of measurements of time averaged ICF of light scattered by single scattering volumes for different values of the scattering vectors. The horizontal axis has been normalized by dividing τ by the initial decay time $(D_c q^2)^{-1}$ ($D_c \approx 2.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$). It is seen that within the experimental accuracy the data points cluster around a unique curve. The

experimental contrast in the ICF, i.e. the ratio $g^{(2)}(q, 0)/g^{(2)}(q, \infty)$ is ~ 1.85 , that is the same value as for a test ergodic solution

Figure 5 shows the comparison between the average curve fitting the data of figure 4 and the ensemble averaged ICF obtained at $\theta = 90^\circ$ on the same system by summing, prior to normalization, the ICF obtained from different scattering volumes in the sample. If one excepts a small deviation in the high τ limit, the two curves can be superimposed on each other quite well

The last test for the ergodicity of the gels consisted in comparing ICF obtained respectively from a gel and a solution at same C_p and α . This test is illustrated by figure 6. We observe that the ICF corresponding to these two systems almost coincide. It must be noted that, due to the very low scattering intensity of the samples at high ionization degree ($\alpha = 0.3$), the data of figure 6 have been obtained by collecting scattered light on several coherence areas. This results in a lowered contrast

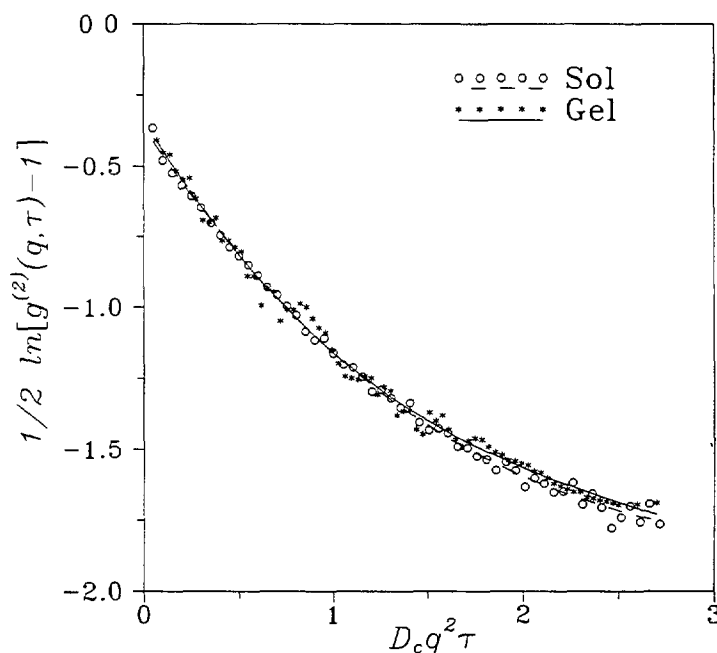


Fig. 6 — Comparison of the normalized time averaged ICF relative to a gel and a solution with $C_p = 0.707$ M and $\alpha = 0.3$, $\theta = 90^\circ$

3.2 SHAPE OF THE AUTOCORRELATION FUNCTION — Generally, dynamic light scattering experiments on gels are analyzed through the approach proposed by Tanaka *et al* [20]

In this approach, the gel is treated as a viscoelastic continuum medium in which the scattering is due to concentration fluctuations, the scattered field being assumed to be a zero-mean complex Gaussian variable. Such a model which neglects all problems associated with non ergodicity doesn't differ basically from that of semi-dilute solution of long flexible chains. The ICF is predicted to be single exponential with a decay rate $2 D_c q^2$ where D_c is the cooperative diffusion of the network.

The measurements performed on PAA gels give a rather non exponential ICF (cf. Fig. 5). Cumulant analysis provides values of the second normalized cumulant $0.1 \leq v \leq 0.25$. Such a

result could be indicative of an effect of the restricted motion of the scatterers [16]. As we have observed the same non-exponentiality in polymer solution and gels (cf. Fig. 6) we can discard such an explanation. One must however remark that for low ionization degrees the difference between the intensity correlation functions for a gel and a solution is more marked (cf. Fig. 7). This might be due to the fact that at low ionization degree the contribution to the osmotic compressibility from the neutral polymer becomes important. Therefore, effects of size polydispersity of the polymer might become more apparent in the autocorrelation function of light scattered from solutions than in the one relative to the gels.

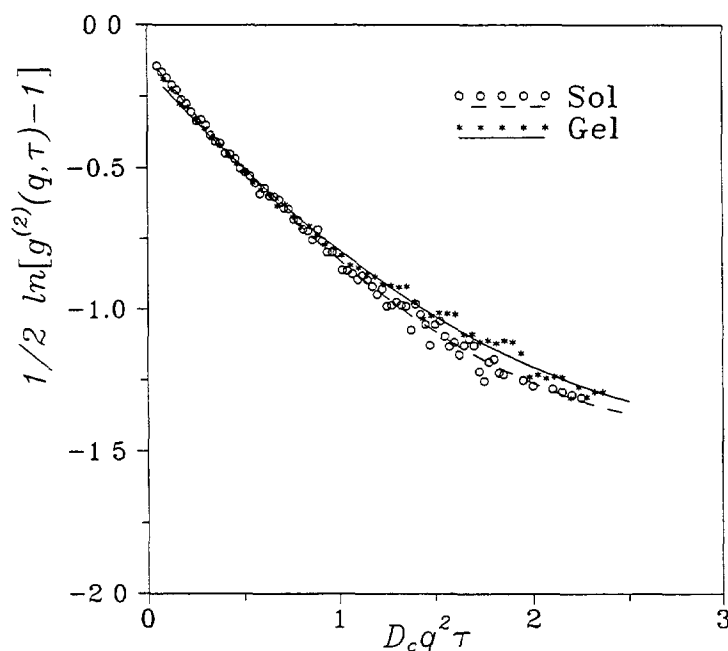


Fig. 7. — Comparison of the normalized time averaged ICF relative to a gel and a solution with $C_p = 0.707$ M and $\alpha = 9 \times 10^{-3}$, $\theta = 90^\circ$.

The ensemble of the above results shows that the gels of PAA behave as ergodic media. This means that the scattering elements, although localized, may be able to achieve quite large displacements so that the scattered field can be considered as a zero-mean complex Gaussian variable. Another important result is that the solutions and the gels behave similarly with respect to light scattering experiments. In particular, and contrary to the previous studies on solutions of polyelectrolytes [21], there is no evidence of a slow mode in the autocorrelation function.

4. Effect of the polymer concentration and of the ionization degree on the cooperative diffusion coefficient of gels and solutions.

From the cumulant analysis of the autocorrelation function of scattered light, we can determine the average cooperative diffusion coefficient D_c .

The variations of D_c with α for both solutions and gels at $C_p = 0.707$ M are shown in figure 8. One sees that at high ionization degree the data for both systems coincide. On the other hand, for $\alpha \leq 0.1$ the cooperative diffusion of D_c is larger for solutions than for gels.

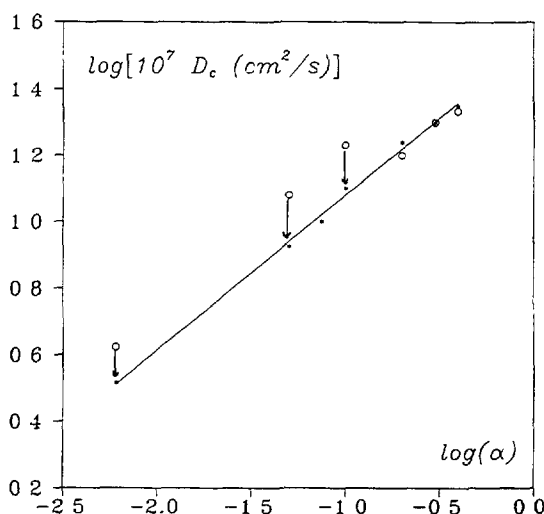


Fig 8 — Log-log plot of D_c versus α for gels and solutions. The arrows indicate the data relative to the gels, corrected for the excess of the intensity scattered from the gel with respect to that from the solution (see the text).

This behavior is quite consistent with the results of the scattered intensity shown in figure 3 and discussed in paragraph 2. According to the Tanaka's model the cooperative diffusion can be expressed in terms of the longitudinal modulus M and the friction coefficient per unit volume f [20]

$$D_c = \frac{M_{os}}{f} \quad (11)$$

The scattered intensity is inversely proportional to M_{os} so that D_c can be written as

$$D_c \sim \frac{1}{I_s f}. \quad (12)$$

If we correct in figure 8 the data relative to solutions with $\alpha = 8.9 \times 10^{-3}$, $\alpha = 5 \times 10^{-2}$ and $\alpha = 10^{-1}$ by the ratio $\Delta I_{sol}/\Delta I_{gel}$ obtained in figure 3, we can observe that, within the experimental accuracy, the corrected data fall on the line describing the results of gels (cf Fig. 8). Therefore, we can conclude that the difference in the behavior of gels and solutions at $\alpha \leq 0.1$ can be attributed to the sole effect of the osmotic compressibility, the friction factor remaining unaffected. This is best illustrated by the figures 9 and 10 that show the variations of f , as calculated by combining the measurements of D_c and I_s , with α and C_p . From these data one obtains empirically the following relationship, valid for both gels and solutions. $f \sim C_p^{-1.5} \alpha^{-0.5}$. A recent calculation using the Kubo's relation between the friction coefficient and the pair correlation function $g(r)$ yielded for weakly ionized semi-dilute solutions in poor solvent, an analytical expression of f [24] that can be approximated by this empirical power law.

In figure 11 are presented the variations of D_c versus C_p for solutions of PAA at $\alpha = 0.1$ and $\alpha = 0.3$ respectively. A net crossover can be observed at a concentration $C_{p_{max}}$ that increases with α . D_c decreases in the high concentration side as it is also observed for gels. In the low concentration range it can be assumed that one probes the translational

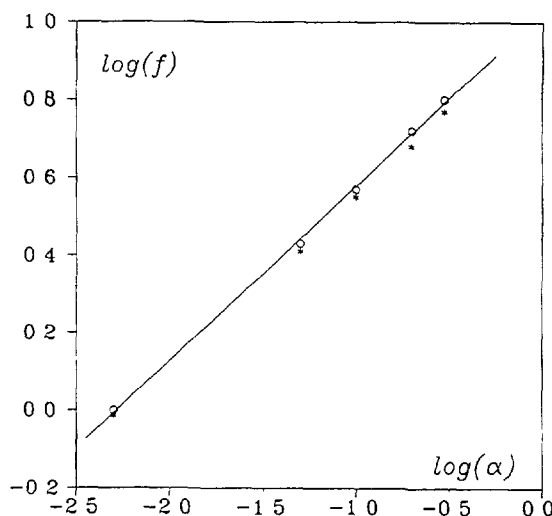


Fig 9 — Log-log plot of f versus α for gels and solutions at a concentration $C_p = 0.707$ M (O) solutions, (*) gels

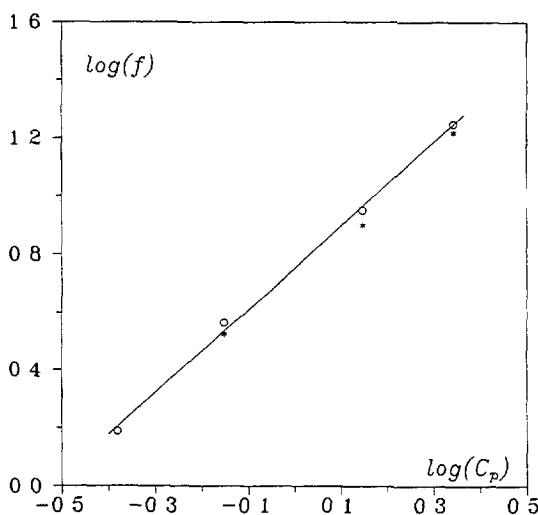


Fig 10 — Log-log plot of f versus C_p for gels and solutions at $\alpha = 0.1$ (O) solutions, (*) gels

diffusion of molecules, the high positive slope of $D_c(C_p)$ being due to the strong repulsive electrostatic forces. Therefore the maximum of D_c could be related with the crossover c^* between dilute and semi-dilute regimes. As a matter of fact, for a given α , the formation of gels at concentrations lower than $C_{p_{\max}}$ is very difficult and requires a larger amount of initiator. A priori it seems surprising that $C_{p_{\max}}$ increases with α since at higher α the chains are more extended and one would expect a smaller value of the crossover concentration. However, it is known that the average molecular weight of the partially neutralized PAA decreases as α increases because the rate constant k_p of the acidic form is larger than that of

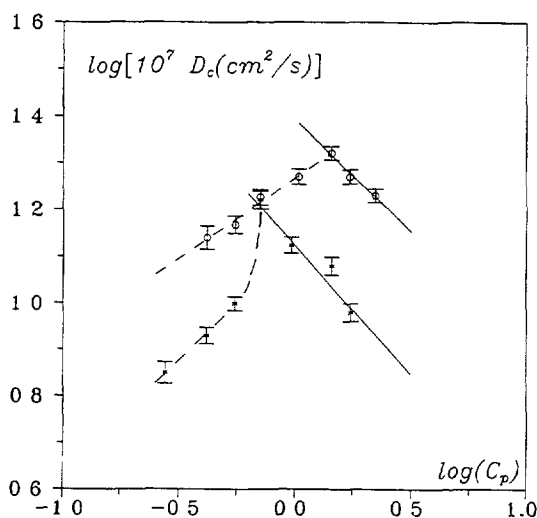


Fig. 11 — Log-log plots of D_c versus C_p for solutions at $\alpha = 0.1$ (*) and $\alpha = 0.3$ (O). The straight full lines represent the results relative to the gels.

the polyacrylate salt [22]. Such effect confirmed by our measurements of molecular weight (cf. sample preparation) explains the result of the figure 10.

Conclusion.

The most striking result of this study concerns the disappearance of inhomogeneities in gels when electrical charges are created on the chains of the network. This was interpreted as a consequence of a rearrangement of the chains in order to form density fluctuations with a spatial period much shorter than the wavelength of the light. An estimate of this period is given by the position of the peak observed in the small angle neutron scattering pattern. This optical transparency allowed us to test possible non ergodic behaviors of gels with respect to DLS experiments. Such non ergodic effect, predicted by Pusey and van Megen [16] have been verified experimentally by Joosten *et al.* on systems of particles trapped in a gel [23]. On the other hand, the interpretation of the DLS experiments on non labelled neutral gels is ambiguous as the scattering from inhomogeneities superimposes on that from the collective fluctuations of the network. In the latter case the ensemble of the results obtained for gels of different kind suggest that the inhomogeneities can be considered as oscillators trapped in the swollen matrix. The signal arising from such inhomogeneities is much larger than that scattered by the network diffusive modes. When looking at short time scale, the time autocorrelation function can be analyzed by assuming that the signal associated with the fast collective fluctuations is heterodyned by the signal due to the inhomogeneities, without significant effect of restricted motion of the scatterers. This is the way, most of the DLS data on gels have been analyzed [12]. However, one can also use the procedure proposed by Joosten *et al.* [22] in which case one probably probes the restricted motion of the inhomogeneities.

Here, the gels investigated do not show up any inhomogeneities and only the scattering from collective diffusive modes is probed. The results presented show that there is no visible non ergodic behavior which means that the effect of restricted motion of scatterers is negligible. This is also evidenced by the comparison between the DLS results obtained in gels

and in solutions. The general features of the autocorrelation function for both systems are very close. A fundamental explanation of the above finding is still lacking, there is still no microscopic theory for the intermediate scattering function $f(q, t)$ of a gel.

The variations with the ionization degree and the polymer concentration of the friction coefficient are very similar in gels and in solutions. These variations are in semi-quantitative agreement with the theoretical predictions based on recent models for weakly ionized semi-dilute solutions in a poor solvent [24, 25].

Acknowledgements.

We thank P. Pusey, J. Joosten, J. F. Joanny and E. Raphaël for very helpful discussions.

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