Cambridge University Press
978-1-107-41018-3 - Macromolecular Liquids: Materials Research Society Symposium Proceedings: Volume 177
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PART I

Polymers

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STRUCTURAL PROPERTIES OF COVALENTLY CROSSLINKED GELS AS PROBED BY SCATTERING TECHNIQUES

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ABSTRACT

This paper reviews some characteristic results obtained by scattering techniques in two sorts of swollen covalently crosslinked networks : neutral networks swollen by a good solvent and weakly ionized gels. For neutral networks swollen at saturation, the local conformation of the chains was found to be the same as in semi-dilute solutions, whereas some concentration inhomogeneities are observed at larger scale. Ionized gels are characterized by a peak of the structure factor and the absence of long range stationary concentration fluctuations at the concentration of preparation of the gels.

I. INTRODUCTION

In this paper, we consider gels consisting of tridimensional networks of flexible polymeric chains covalently crosslinked and swollen to a large extent. We address some of the problems specific of this network structure.

By reference to a semi-dilute solution of linear chains, the presence of crosslinks between chains reduces the number of conformations available for the polymer chains and therefore confers new properties to the material. Among these properties, one can quote in particular :

i) The onset of a zero frequency shear elasticity

ii) The presence of microscopic heterogeneities associated with random or non random crosslinking

iii) The non ergodicity of the correlation function of the intensity of scattered light in a dynamic light scattering experiment [1].

While the above properties are specific of the network nature of the gel, the local conformation as well as the high frequency dynamic properties are rather characteristic of a semi-dilute solution and are well described by the scaling theories [2]. This explains why two different approaches, based, one on the rubber elasticity theory [3], the other on the scaling concepts used for semi-dilute solutions [4][[5][2], have been proposed.

In the following, we review first some of the characteristic features of the non-ionic gels swollen by a good solvent. Then we discuss recent results obtained for gels whose swelling by water is enhanced by the presence of electric charges on the polymer chains.

II. NEUTRAL GELS SWOLLEN BY A GOOD DILUENT

II-1 Short Range Conformation and Deformation Mechanism

In the classical description of gels [3], the setting of tie-points between chains, followed by the swelling of the resulting network, is expected to induce a noticeable modification of the local conformation. Referring again to the semi-dilute solutions, a change of concentration produces a slip of the chains with respect to each others. On the opposite, it is generally assumed that, upon swelling, the elementary chains of a gel, i.e. the chains segments between two first neighbor crosslinks, are

Mat. Res. Soc. Symp. Proc. Vol. 177. ©1990 Materials Research Society

noticeably stretched. This description, when expressed in terms of the free energies of dilution of the polymer and of extension of the chains assumed to be Gaussian springs, leads to the right orders of magnitude for the swelling degree and the shear modulus of the gels. However, when going into the detail, one observes in general persisting discrepancies between experimental data and theoretical predictions. In fact, the primary issue is that of the deformation mechanism that has been the subject of a long lasting debate [6]. The two existing main models of deformation agree on the basic assumption of an "affine" displacement (in the macroscopic deformation) of the mean positions of the crosslinks, but they disagree on the effect of the fluctuations of these points around their mean positions. In the strict "affine" model [3][6-8], the fluctuations are assumed to be reduced at naught, or affinely changed in the macroscopic deformation. On the other limit, the network model assumes large fluctuations independent of the macroscopic state [6][9-10].

To try to discriminate between these models, small angle neutron scattering (SANS) experiments have been carried out on Polystyrene, Polyacrylamide and Polydimethylsiloxane gels. A large part of them are reviewed in refs. [5][11][12].

Here, we would like to recall some of these experiments, that we find significant and easy to discuss. Polystyrene networks containing a fraction of deuterated elementary chains and swollen by benzene were investigated in order to determine the variations of the radius of gyration R_G of these labelled chains upon a change of swelling [13]. These gels were obtained by end-linking of well defined precursor chains ($M_w \simeq 26.000$, $M_w/M_n \leqslant 1.2$). The crosslinks consisted in divinylbenzene molecules reacting together and forming nodules of unknown functionality. To obtain different stages of swelling, the gels were immersed in solutions at different concentrations of very long polymer chains of the same chemical nature as the network. With this procedure, the local polymer-solvent interactions are not affected by the change of swelling. The experimental results are reported in Fig.1. It is seen that, for swelling degrees of the gel varying by a factor of ~ 4, the radius of gyration remains almost constant and, within the experimental accuracy, the same as that of the free chain in the same environment (e.g. 60 Å, in pure benzene).

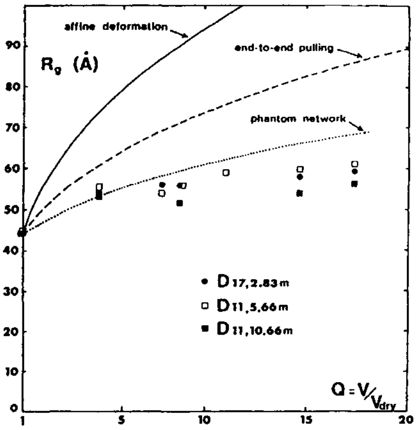

Fig. 1. Radius of gyration of the labeled chains of the network as a function of the swelling degree. D_{17}, D_{11} refer to the ILL spectrometers used for this experiment

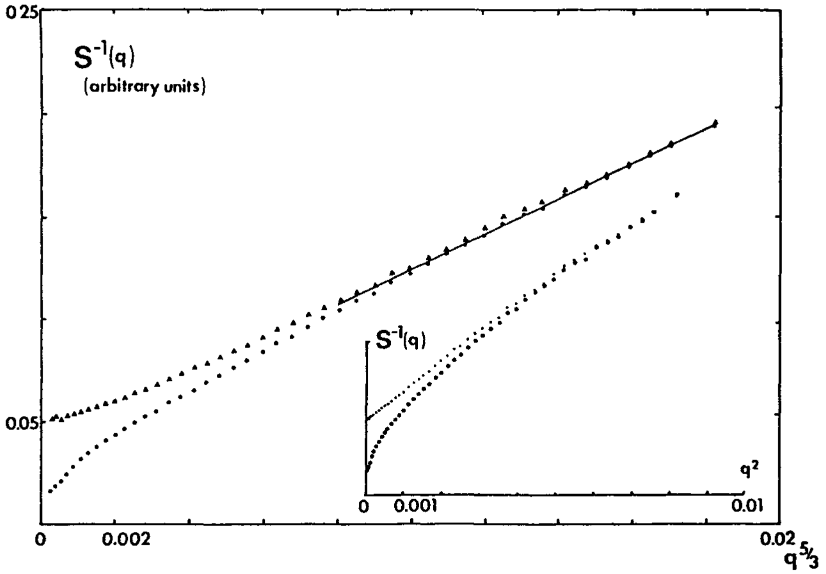

Fig.2. Plot of $S^{-1}(q)$ vs. $q^{5/3}$ for a totally deuterated PS network swollen at equilibrium in CS_2 and the corresponding semi-dilute solution at the same concentration. In the inset, plot of $S^{-1}(q)$ vs. q^2 in the $q\xi < 1$ regime. From [5].

Thus, no real "network effect" on the conformation of the chains at short scale was detected in this experiment. In other words, the deformation might be even weaker than the one corresponding to the "phantom" limit in the case of a swelling-deswelling process. Even though the above statement has been controversed [14], it remains that the deformation of the chain is far weaker than that corresponding to the strict affine model. Strongly non affine mechanisms like network folding at scale larger than the mesh [15][5] are likely to be involved in the mechanism of gel swelling.

Another type of experiment consists in labelling the whole network with respect to the solvent and to compare the scattered signal to that of a semi-dilute solution at the same concentration. A typical result is shown on Fig.2 [5]. The gels were formed by statistical crosslinking of long primary chains, under γ irradiation in a θ-solvent at a polymer concentration of 0.1 g.cm^{-3}. The obtained networks were washed and swollen at saturation in CS_2. Let us first focus on the results relative to the solution. When plotting the inverse of the scattering intensity $I(q)$ versus q^2 (q being the scattering vector amplitude), one gets a straight line behavior (for not too large q values) which allows for the determination of the screening length ξ_{sol} (insert of Fig.2). This means that the scattering intensity fits the Ornstein Zernicke type form [16] $I(q) \sim (q^2 + \xi_{sol}^{-2})^{-1}$, for $q\xi_{sol} < 1$. In the exemple presented here, ξ_{sol} is approximately equal to 20 Å. For larger values of q ($q\xi_{sol} > 1$), one expects to probe the inside of the "blobs" of size ξ_{sol}. If ξ_{sol} was infinite, one would get $I(q) \sim q^{-1/\nu}$ in this range of q (ν being the excluded volume exponent, approximately equal to 3/5). This is easy to predict using the language of fractals [17]. When a system is self-similar at scales of distances smaller than L, it is known to scatter like $I(q) \sim q^{-D_f}$ for $qL \gg 1$, D_f being its fractal dimension. In the case of a polymer chain D_f is equal to $1/\nu$, by definition ; this leads to the asymptotic behavior given above.

Here, $\xi = L$ is not very large. As a result, I(q) is expected to tend only very smoothly towards the asymptotic behavior. More specifically, one expects $I(q) \sim (q^{1/\nu} + K)^{-1}$, K representing a cut-off associated with the finite size of ξ_{sol}.

The scattering by a semi-dilute solution is in good agreement with the above q dependence since a straight line behavior is obtained at the larger q values when plotting $I^{-1}(q)$ versus $q^{5/3}$.

We turn now to the gel. One observes that, for q values such as $q\xi_{sol} > 1$, the scattering coincides almost perfectly with that of the solution. This means that, as in the preceding experiment, no local extension of the chains is detected. As a matter of fact, significantly stretched chains would have a fractal dimension larger than $1/\nu$ (and closer to 1). $I^{-1}(q)$ versus $q^{5/3}$ would not be then linear. Thus, we have here a second indication of the weakness of the "network effect" on the chain statistics. Nevertheless, important things seem to happen at larger scales. The difference between the scattering from the gel and that of the solution is indeed quite large for lower q values. The scattering intensity from the gel is much more important ($I^{-1}(q)$ is smaller). This excess of scattering has been attributed to the presence of crosslinking heterogeneities. The presence of such defects has been inferred previously, from the results of light scattering [5][18] and solvent permeation [19] experiments. This phenomenon is discussed in the next paragraph.

II-2 Crosslinking heterogeneities

The representation $I^{-1}(q)$ versus q^2 is not well adapted to a further discussion of this problem. Quite often, it is more illustrative to plot log(I(q)) versus log(q). In the case of a semi-dilute solution, the two regimes introduced above appear well separated. We consider here a solution of polystyrene ($M_w \simeq 700.000$) in deuterated toluene at a volume fraction equal to $5.6\ 10^{-2}$ (see Fig.3) [20] ; ξ_{sol} has been found equal to 18 Å using the preceding representation. In the present logarithmic plot, the signal is almost flat for $q\xi_{sol} < 1$. This reflects the quasi-compactness of the system at these scales of distances ($> \xi_{sol}$). For $q\xi_{sol} > 1$, the curve tends towards a straight line of slope -5/3, as expected : this corresponds to the intra-chain self similar regime, which is quite short, since ξ_{sol} is rather small. At still larger q values ($q \gtrsim 2.10^{-1}$ Å^{-1}), the experimental curve seems to depart again from this straight line behavior. This is not surprising since one probes there the range of scales corresponding to the inside of the statistical units. We don't discuss any longer this regime, because the signal over noise ratio is very poor for such high q values.

On the same figure is plotted the scattering intensity from a polystyrene gel swollen at saturation in deuterated toluene at the same polymer concentration as that of the solution. This network has been obtained by random crosslinking of very long precursor chains ($M \simeq 10^6$), at a polymer volume fraction $\varphi_c = 0.1$. The reaction employed was a Friedel and Crafts type, with $C_6H_4(CH_2Cl)_2$ molecules acting as interchain tie-points, with $SnCl_4$ as a catalyst. For more details see refs.[21][22] and a forthcoming paper [23]. At saturation, this gel is overswollen by a factor 1.8 (in volume) with respect to its preparation conditions. As in the preceding experiments, no local extension of the chains associated to the swelling can be detected, since the scattering curve of the gel and of the solution gather perfectly for $q\xi_{sol} > 1$. On the opposite, for $q\xi_{sol} < 1$, the two curves appear to be very different from each others : the intensity is much larger for the gel than for the solution. As for the solution, a pseudo plateau region seems to exist for the gel, likely indicating compactness beyond a certain scale. The value $\tilde{q}$ of the scattering vector amplitude at which the signal starts to level off gives an estimate of this scale of compactness (that we call ξ_{gel}), by assuming $\xi_{gel} = 1/\tilde{q}$. Under this definition, ξ_{gel} is much larger than ξ_{sol}, a behavior which is not expected from the classical description of flexible gels. As a matter of fact, if the only mechanism of swelling was a homogeneous stretching of the elementary strands, the scale of compactness should vary less, under a given change of concentration, than in a comparable solution. As a result, ξ_{gel} should be smaller than ξ_{sol}. Something different is happening here, which indicates that ξ_{gel} should not be considered as the limit of the intra-elementary chain behavior. A model that we present below provides some further indications on what this intermediate structure can consist in, in the case of randomly crosslinked gels.

Another important point is to know whether this excess of signal originates in the crosslinking itself or in the overswelling with respect to the preparation state. The same Friedel and Crafts crosslinking has been performed on deuterated polymer, and the scattering signal has been investigated directly in the reaction bath. It is only when one approaches syneresis that an excess of signal appears. Therefore, the observed strong increase of concentration inhomogeneities seems to constitute, at least, a part of the swelling mechanism. It must be stressed that this does not mean that crosslinking heterogeneities do not exist in the reaction bath. They can be masked, as it is shown in the next paragraph.

Such type of experiments have also been performed for gels obtained by end-linking [20]. In that case, the situation is less simple. Strong heterogeneties of polymer concentration exist at saturation, as well as in the reaction bath. The form of the scattering signal is more complicated and up to now, it has not been possible to determine unambiguously an estimation of ξ_{gel} in these systems.

II-3 A Model of Crosslinking Heterogeneities in Statistically Crosslinked Gels [20][24]

This model addresses a simplified situation, namely a semi-dilute solution of very long chains, crosslinked almost instantaneously. The basic idea is that the effective inter-chain tie-points are statistically distributed among the inter-chain contact points pre-existing in the solution. Thus, this process can be described not only as a gelation of chains , but also as a percolation. The perfectly random arrangement of crosslinks produces regions which are richer or poorer in crosslinks. In a frequent regime of crosslinking densities, the rich-in-crosslinks regions consist of clusters of connected blobs, which are entangled in each other. (cf. Fig. 4a). According to the percolation model, these clusters are fractal, and can be quite large. They are however undetectable in the reaction bath (even if they were labelled), since cluster-cluster correlations exactly compensate the intra-cluster ones.

The situation is different when adding some solvent to the gel. The clusters of connected blobs are less deformed than the gel on an average, because they are more densely crosslinked (see Fig. 4b). As a result, smaller clusters are expelled from the inside of bigger ones, creating regions of lower concentration. The correlation length ξ_{gel} can be viewed now as the typical size of clusters which are not entangled with bigger ones. Because of the polydispersity of the clusters, one expects a strong dependence of ξ_{gel} on the dilution degree ($\xi_{gel} \sim C^{-5/3}$, see details in ref.[24]). Regarding the scattering, intra and inter cluster correlations are no more balanced. Therefore, for $q\xi_{gel} > 1$, one probes the fractal dimension of the clusters of frozen blobs, with a certain correction due to the cluster polydispersity. Altogether, in the range $1/\xi_{gel} < q < 1/\xi_{sol}$, one expects $I(q) \sim q^{-1.6}$. This dependence is in good agreement with the experimental curve referring to the randomly crosslinked gel. More precise

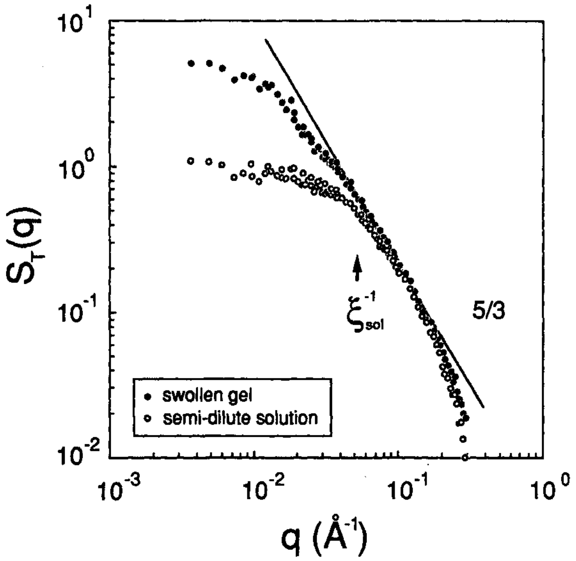

Fig.3. Absolute total intensities scattered by a gel swollen to saturation and a semi-dilute solution of large molecular weight chains ($M = 10^5$), of polystyrene at the same volume fraction ($\varphi = 5.6\ 10^{-2}$). The solvent is deuterated toluene. The curves are superposed without the help of any adjustable parameter. Data from ref. [20].

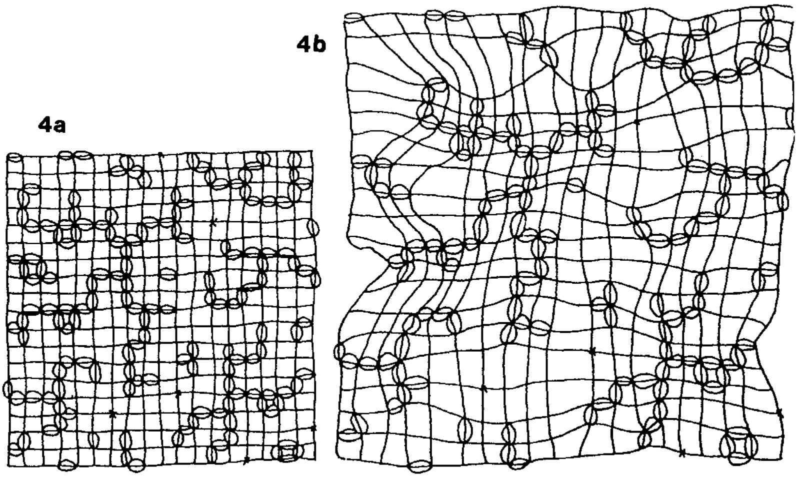

Fig. 4a. Schematic representation of a statistically crosslinked solution, in the reaction bath (well above the gel point of the chains, but a little below the gel point of the blobs). x isolated crosslink, ⊖ frozen blob (i.e. blob limited by 2 junctions). From refs. [20][24].
Fig. 4b. Same as Fig. 4a, but overswollen with respect to the preparation conditions. From refs. [20][24].

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comparisons are now underway, and seem to indicate reasonably agreement too. In any case, the important point to hold from this model is that crosslinking inhomogeneities are not necessarily well separated from each other. Depending on the synthesis conditions, they can grow in an entangled manner and separate, at least partially, upon swelling.

III. IONIZED GELS

The studies of the structural properties of ionic networks are rather scarce, whereas the conformation of polyelectrolyte chains in solutions has been thoroughly investigated by means of scattering techniques [25][26]. Here, we report recent results obtained by SANS and Light Scattering techniques on partially ionized poly(acrylic acid) (PAA) gels [27]. The gels were prepared by a standard radical copolymerization of acrylic acid and N-N'-methylene bisacrylamide in aqueous solutions. A fraction of acrylic monomer was neutralized by sodium hydroxide prior to polymerization. The polymer concentration C in the gel was 0.707 M (50 g/L) and the ionization degree α, i.e. the ratio of the number of carboxylate groups to the total number of monomers was varied between 0.025 and 0.4. The samples were studied at the concentration of preparation without further swelling.

III.1. SANS measurements

The experiments were performed on spectrometer PACE in Laboratoire Léon Brillouin. Solutions with same compositions as the gels swollen by D_2O were taken as background samples.

Scattering curves for samples with different ionization degrees are reported in Fig.5. One observes for the weakly ionized gels a peak of the structure factor, whose amplitude decreases as the ionization degree is increased. In the high q range the scattered intensity becomes independent of α and decreases as q^{-a} with $a \simeq 1.7$.

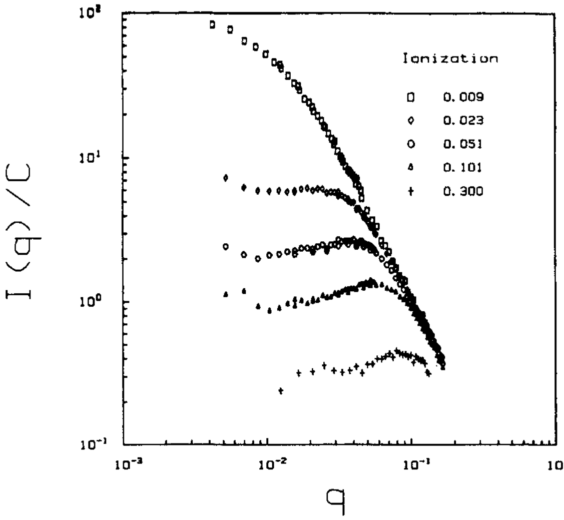

Fig. 5. Variation of the structure factor of the ionic gels with the ionization degree α for a given polymer concentration C = 0.707 M.

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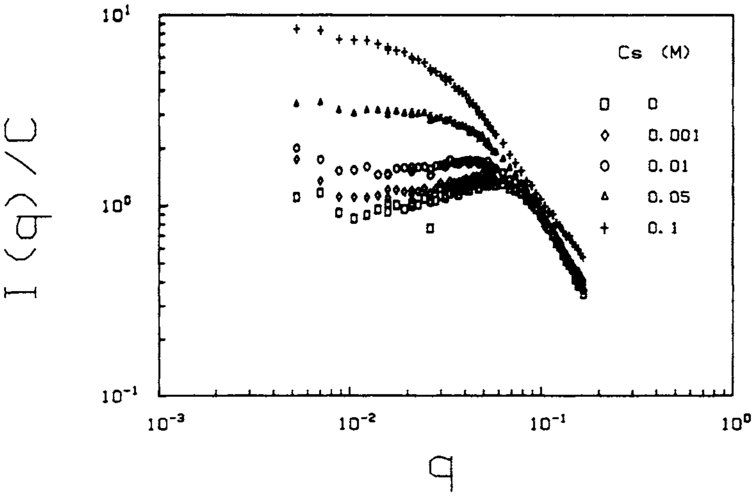

Fig. 6. Effect of the added salt concentration on the structure factor. Polymer concentration is C = 0.707 M and ionization degree is $\alpha \simeq 0.101$.

The influence of added salt (NaBr) on the scattering intensity doesn't change the intensity in the high q range (cf. Fig.6). On the other hand, the peak position shifts to smaller q values as the concentration C_s of added salt increases. Eventually, the peak disappears at high salt content and I(q) decays monotonically to zero.

The range of ionization degrees for which a peak appears in the scattering curve corresponds to the weak coupling limit, since the contour length between two successive charges on the chain is larger than both, the Bjerrum length and the Debye-Hückel length. Recently a model has been proposed to describe the structure of semi-dilute solutions, for weakly charged polyions having an amphiphilic character, due to a poor solubility of the polymer backbone in water [28][29]. 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 wavevector q^* that fixes the period of the mesophase.

In the gels investigated here, the water is a rather good solvent of the PAA chains but the methylene bisacrylamide crosslinks have a very limited solubility in water. This confers an amphiphilic character to the network and it has been postulated that the crosslinks could tend to cluster, thus forming dense polymer regions [27][19]. The electric charges, that are mobile along the chains, and the counterions would be expelled from the clusters of crosslinks and occupy the dilute regions. The peak of I(q) observed experimentally would then have the same origin as the one predicted for semi-dilute solutions of weakly ionized polymers in poor solvent. In this model, the variations of the peak wavevector q^* as a function of polymer concentration and ionization degree are given by :