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Comparison Between the Elasticity of Polyacrylamide and Polyacrylic Gels

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Abstract. — We measured the Young modulus E of polyacrylamide and polyacrylic gels as a function of the crosslink and polymer concentrations. We found that the variation of E with these two parameters is completely different for the two kinds of gels. For the polyacrylic gels, E is an increasing function of the crosslink and polymer concentrations. However, in the case of the polyacrylamide gels, E increases with polymer concentration but not always with the crosslink concentration. For low polymer concentrations, E may saturate or exhibit a maximum when increasing the crosslink concentration. We proposed qualitative interpretations to explain this different behavior.

1. Introduction

The physical properties of gels and in particular their elastic properties were and are still the subject of intense investigations [1]. In this paper we focus our attention on the elastic behavior of two different gels: polyacrylamide and polyacrylic gels. It is already known [2,3] that the elastic modulus G as a function of the crosslink content behaves differently for the two gels but it does seem that an extensive study of their elastic properties were made. The elasticity of these gels are very often presented among other properties and are not investigated in detail. In particular, the dependence of G with the polymer concentration is not very well known. The purpose of this paper is to investigate the dependence of G with the two basic parameters which control it: the crosslink concentration c and the polymer concentration p .

These two kinds of gels are examples of two basic network defects: inhomogeneities (polyacrylamide gels) and entanglements (polyacrylic gels). Recently, these two types of defects have been studied theoretically by Vilgis [4] and as we shall show, our conclusions are not always in accordance with his theoretical predictions.

We recall two important points in the theory of the elastic modulus of a gel. First is the coefficient C_0 which appears in the simple elastic modulus formula:

$$G_1 = C_0 c k T \quad (1)$$

In (1), k is the Boltzman constant and T the absolute temperature. The basic assumption in (1) is that there is no interaction between chains. There is a large amount of work devoted to the determination of C_0 [5]. For a functionality of four (as in our case) C_0 varies between 1/2 and 1/4. However, the important point is that G_1 has a linear dependence with c and is independent of p . In (1), it is understood that c is the effective crosslink density, which is not necessarily equal to the total crosslink density since dangling ends and loops do not contribute to the elastic modulus. The second point is the interaction between the chains which can be seen as closely packed blobs [6]. The influence of the chain interaction on the elastic modulus is a difficult problem. In general, the elastic modulus is written as the sum of two contributions $G = G_1 + G_2$, where G_1 is given by (1) and G_2 is the new contribution. The concept of entanglements [4] is largely used and has the advantage of giving a simple physical picture of the chain interaction. Vilgis [4] proposed recently a method to calculate the elastic modulus as a function of c and p : G is no longer a linear function of c as in (1), but remains an increasing function of c .

It is well-known that polymer gels are in general inhomogeneous [4, 7–10]. The accepted picture is the existence of static inhomogeneities in which there are fluctuations in the crosslink molecules densities, with appearance of regions rich and others poor in crosslink molecules. In the case of the polyacrylamide gels, this picture is largely accepted as conclusion from different experimental results [3, 11–13]. The recent results of Cohen *et al.* [3] are very interesting. They analyzed their SAXS by means of a simplified structure of the gel seen as a matrix with spherical inclusions rich in crosslink molecules. The radius of the inclusions is the mean size of the clusters with high crosslink molecule content. We mention that Weiss *et al.* [12] interpreted the results of permeation experiments using the same model.

2. Experiments and Results

We measured the Young modulus, which is equal to three times the shear modulus, varying the two important quantities. the crosslink concentration c and the polymer concentration p .

Fig. 1. — Young modulus of the polyacrylamide gels as a function of the crosslink concentration for different polymer concentrations.

Fig. 2. — As in Figure 1 for polyacrylic gels

Both kinds of gel were prepared following essentially the same method with small differences. A given quantity of monomers (acrylic acid or acrylamide) was put in distilled water with the chosen amount of the tetrafunctional agent as crosslink (N,N' - methylene bis acrylamide) with initiators. For the polyacrylic gels we took ammonium persulfate only, while for the polyacrylamide gels we took ammonium persulfate and tetramethylethylen (TEMED) [7]. In the case of polyacrylic acid, nitrogen was bubbled in the solution to remove oxygen which could inhibit the reactions. The polyacrylamide gels are ready in about 30 min. at ambient temperature, but the polyacrylic gels need to be heated at 70 °C for 8 h. The samples have a cylindric shape (diameter 2.3 cm and length 3 cm). In the preparation of the polyacrylic gels, we followed very closely the procedure indicated by the authors of reference [2]. With no addition of salt (NaOH) or acid (HCl), they give a degree of dissociation of $10^{-2} - 5 \times 10^{-3}$. From their measurements of the elastic modulus as a function of α (up to $\alpha = 0.6$), one can conclude that our gels are practically neutral.

The measurements were made on the samples as they were prepared with a home built apparatus. We impose a given deformation (compression) by moving a metallic cylinder by means of an eccentric wheel. The frequency of rotation is 0.3 Hz, in the range of frequency for which the Young modulus is independent of the frequency. The force is measured from the signal given by five piezoelectric elements put in serie below the sample. We choose the linear

regime of the curve stress-strain to determine the Young modulus.

In Figures 1 and 2, we show the curves $E(c)$ for different polymer concentrations. The concentrations in polymer p and in crosslink c are given in percentage of the solution (monomer + solvent), in volume: $p = 10\%$ means 10% of polymer and 90% of water in the solution. One sees immediately the difference between the two ensembles of curves and in each case one can distinguish several regimes. For the polyacrylamide gels one has four regimes: a) for small values of c ($c < 0.1\%$) and whatever the value of p , E increases with c . b) for larger value of c and $p < 10\%$, E saturates and becomes independent of c . c) for large c and intermediate values of p ($10\% < p < 18\%$) E exhibits a maximum. d) for large c and large p ($p > 18\%$) E increases with c sometimes with an inflexion point. The maximum in E was already mentioned [3, 13] but it seems the different regimes of the Figure 1 were not observed before.

The Young modulus of the polyacrylic gels behaves very differently. It is always an increasing function of c and p . For low value of p (about 8%), E increases linearly with c and again for the largest value of p . Between $p = 8\%$ and $p = 14\%$ there is a gradual passage from the behavior at low p to that at larger p .

3. Interpretation and Discussion

The problem we want to address is the dramatic difference in the behavior of the two kinds of gel. The two kinds of gel were prepared following the same procedure. At the beginning the monomers are put in the solution with the crosslink. The gel is formed as a consequence of two reactions: the monomer-monomer (MM) reaction creating the polymer chains and the crosslink-monomer (CM) reaction giving the network. These two reactions do not take place at the same rate. We shall assume that the rates of the two reactions are different. For the polyacrylamide gels the rate of the CM reaction is much larger than that of the MM reaction. It follows that at first, units of one crosslink molecule and four monomers are formed and only after the chains are made. This process will create regions rich in crosslink agent and others with a lower density. The assumption regarding the different rates of the MM and CM reactions is confirmed in reference [13]. In the case of reaction the polyacrylic gels, we assume the opposite situation: the rate of the MM reaction is larger than that of the CM reaction. Consequently the polymer is formed first and the process of crosslinking takes place slowly.

One consequence of our assumption regarding the different formation of the gels is that in the case of polyacrylic gels, the fluctuations in the crosslink density will be small and the elastic modulus can be seen as the average of the moduli in the different regions of the gel. We shall try to explain their elastic behavior by the influence of the entanglements.

However, in the case of the polyacrylamide gels, the crosslink density fluctuations are so strong that it is not possible to consider the elastic modulus as merely the average of the local moduli. A more appropriate approach is necessary. On the other hand, it is clear that the entanglement contribution (which clearly exists in these gels) cannot explain the saturation or the maximum of $G(c)$.

3.1. POLYACRYLAMIDE GELS. — The effective elastic modulus G_e is that of a composite medium made of stiff inclusions (elastic modulus G_i , relative volume v) and a soft matrix (elastic modulus G_m , relative volume $1-v$). We shall denote $p_i(p_m)$ and $c_i(c_m)$ the polymers and crosslink concentrations in the inclusions (matrix) and we have $p_i > p_m$ and $c_i > c_m$.

We can understand the variation of G with c by a competition between two mechanisms: one giving an increase of G and the other a decrease, when c increases. One of the possible pictures is the following. We can make a reasonable assumption that the depletion process of the matrix (giving $c_m < c < c_i$ and $p_m < p < p_i$) will be stronger and stronger when

c increases. Consequently, G_m will be a decreasing function of c ($dG_m/dc < 0$) and this is the first mechanism for the decrease of G when c increases. At the same time, there is an enrichment of the inclusion in crosslink molecules and polymer giving an elastic modulus of the inclusion which becomes larger and larger when c increases ($dG_i/dc > 0$). It is the second mechanism which gives an increase of G_e .

To be more specific, we shall use the result of the theory of composite materials [14]. For an incompressible material like the gels, the effective elastic modulus G_e is given by

$$G_e = G_m \left[1 + \frac{v(G_i - G_m)}{G_m + 4(1-v)(G_i - G_m)} \right] \quad (2)$$

It is easy to verify that G_e is an increasing function of G_m , G_i and v .

At low c , it is very likely that G_i and G_m are not too different and (2) reduces to

$$G_e = vG_i + (1-v)G_m \quad (3)$$

which express that G_e is the average of the different elastic moduli G_i and G_m . In such a case G_e increases with c and if the chain interaction is weak, the dependence of G_e with c is linear, as experimentally observed. But for larger c , one has $G_i \gg G_m$ (strong fluctuations regime) and the complete expression (2) must be used, when the competition between the two mechanisms takes place.

From the results already published, it is found that (dG_m/dc) < 0 [15] and that (dG_i/dc) > 0 , in accordance with our analysis. It was also found that (dv/dc) < 0 [10, 12], increasing the tendency of G_e to decrease when c increases.

The application of the precedent ideas to the polyacrylamide gels are only tentative and needs a confirmation from a quantitative comparison. It is possible to show from (10) that the inclusions will modify significantly G_e only if the difference $G_i - G_m$ is large enough and v not too small. At the present stage, we do not have reliable values of the relevant quantities for ascertaining the validity of the model.

The model we proposed can be correct only if the stiff clusters are well separated. When the polymer content increases, percolation of dense regions will occur and another model is needed. Above the percolation threshold, the elastic modulus is controlled by the dense phase [16] and not by the soft matrix. In such a situation, one expects a regular increase of G with c as observed for samples with $p > 20\%$. This value of p can be seen as the percolation threshold in this system. Effectively, in three dimensions, the threshold for a disordered system is near 20% [17]. This is to be connected to the finding of reference [12] regarding the tendency of the system to be homogeneous for $p > 16\%$.

To close this section, we mention the prediction of Vilgis [4] about inhomogeneous gels. Vilgis predicts first that the intensity of neutron scattering at small angle will be modified by the inhomogeneities and this was verified experimentally [7]. The second prediction is that the elastic modulus will be that corresponding to the mean values of c and p . This is not in agreement with our experiments in which we found that the elastic modulus saturates or has a maximum when c increases.

3.2. POLYACRYLIC GELS. — We assumed above that these gels are homogeneous and we propose to include explicitly the entanglements to explain their elasticity. First we calculate G_1 from equation (1) with $C_0 = 1/2$. For $c = 0.1\%$ we find $G_1 = 0.75 \times 10^5$ CGS, which corresponds to a Young modulus of $E = 2.25 \times 10^5$ CGS. This value is slightly larger than the measured value for the softest gel (with the smallest p). Since G_1 can be seen as a lower

bound for a gel, it seems that this gel is almost free of entanglements. Furthermore it is the only example of gel with a linear dependence with c as predicted by (1). All the deviations from the straight line of the 7.9% polymer gel are supposed to be due to entanglements.

The slipping model of the entanglements [4] takes into account a certain amount of freedom for the entanglements by means of a parameter η . For $\eta \rightarrow 0$, the entanglements are supposed to be fixed and act as chemical crosslinks. When η increases, the entanglements are less effective. The formula for G (in our notation) is

$$G = \frac{1}{2}kT \left[c + \frac{c_s}{(1 + \eta)^2} \right] \quad (4)$$

where c_s is the entanglement concentration. An equivalent expression for G is

$$G = \frac{1}{2}kTc \left[1 + \frac{2N\alpha}{(1 + \alpha^3 N)^2} \right] \quad (5)$$

Here α is the ratio between the mean distance between entanglements and the length of the statistical segment. N is the number of the Kuhn segments in a chain. Since α is estimated by Vilgis to be of the order of 10^{-1} , and in our gels $N \sim 10^2$, G can be written as

$$G = \frac{1}{2}kTc(1 + 2\alpha N) \quad (6)$$

To compare with the experiment, it is useful to have an expression which includes explicitly the polymer density. First we have $p = 2Nc$ (the Kuhn statistical element is about 1.5 the monomer length [12] and we take it equal to 1 by simplicity). Taking into account that, following Vilgis $\eta = \alpha^3 N$ is a constant of the model we get:

$$G = \frac{1}{2}kT(c + 2^{1/3}\eta^{1/3}c^{1/3}p^{2/3}) \quad (7)$$

Qualitatively, this expression gives a correct description of the elastic behavior of the polyacrylic gels. G is an increasing function of c and p , as observed. If p is small the contribution due to the entanglements may be negligible and when p increases this contribution may be the strongest. From our results we can even get an order of magnitude for η in writing the two following conditions a) for $p = 7.9\%$ the "normal" contribution (G_1) is larger than the entanglement contribution (G_2). b) for $p = 14\%$ we have the inverse situation: $G_1 < G_2$. We found that η must be between 0.18 and 0.13 which are very reasonable values. However, for a quantitative comparison the expression (8) is not adapted to our results. The functional dependence of G with c or with p cannot be described by (8). The conclusion of this analysis are in fact in agreement with Vilgis which does not claim to provide accurate relationships but only qualitative estimates.

4. Conclusion

The elastic behavior of the polyacrylamide and polyacrylic gels is completely different. We relate that to the conditions of their formation. We propose to analyze the results by assuming two different kinds of defects: inhomogeneities in the polyacrylamide gels and entanglements in the polyacrylic gels. We tried to analyze the results following these assumptions but it was not possible to get a complete satisfactorily picture. In the case of the polyacrylamide, we feel that there is a need to get a precise determination of the microstructure of these gels. For the polyacrylic gels, the slipping model of the entanglements gives a good qualitative agreement with the experimental results.

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