Chemical and physical hydrogels: two casesystems studied by quasi elastic light scattering

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Abstract

A chemical hydrogel based on telechelic poly(vinyl alcohol) and a physical synergic hydrogel, xanthan–glucomannan, were studied by means of dynamic light scattering technique. Two different nonergodic methods, due to Pusey et al. (Physica A 157 (1989) 705, Phys. Rev. A 42 (1990) 2161) and Xue et al. (Phys. Rev. A 46 (1992) 6550), were used to obtain the correct dynamic structure factors \( f(q,t) \). Good agreement between the results obtained with the two procedures was found. The behavior of the \( f(q,t) \) for different q vectors is consistent with the hypothesis that the nonfluctuating component in the scattered light is not due to microscopic heterogeneities but to restricted motion of the scatterers. The model of Krall et al. (Phys. Rev. Lett. 80 (1998) 778, Physica A 235 (1997) 19) was successfully applied to both hydrogels to extract the characteristic parameters of the network from the \( f(q,t) \) functions. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Polymer gels are ubiquitous in nature and in many man-made applications, nevertheless their properties are still not easily framed in a unique scheme. This is not surprising because these systems display a coexisting solid-like and liquid-like behavior. Due to the peculiar properties of the solvent, a complex phenomenology appears in hydrogels, whose main component is water. An example of this complex behavior is the notable effect of the ionic concentration in the aqueous phase on the swelling properties of hydrogels. It is now clear that a correct description of these systems can be obtained only by means of a complex set of theoretical and experimental investigation tools.

As far as polymer gels are concerned, referring to the forces involved in the building up of networks, two main classes of hydrogels can be distinguished: (i) chemical hydrogels and (ii) physical hydrogels. In (i), the network of chemical links joining different chains can be obtained by cross-linking bulk polymers or polymers in solution, whereas in physical hydrogels (ii), chains are held together by ionic, hydrogen bonding and/or dipolar interactions. In both cases, the density of cross-links is crucial in determining the properties and applications of the gels, as it is responsible for the swelling behavior and therefore for the combined solid-like and liquid-like characteristics.

A new model [4,5], recently appeared in literature, allows to determine the mechanical and structural properties of fractal gels from their internal dynamics measured by dynamic light scattering (DLS), a comparatively simple experimental technique now used in many laboratories as a standard method for gel characterization. Although this model had been originally devised for colloidal gels, due to its rather general features, it can also be used for polymer hydrogels, allowing to obtain relevant information on their internal dynamics. We have recently shown [6] that the dynamic and structural parameters evaluated on a chemical gel telechelic poly vinyl alcohol (TPVA) using the Weitz model [4,5] compare reasonably well with the results obtained, on the same systems, by means of compression modulus and equilibrium swelling measurements [7,8]. In this note we extend this study to a physical hydrogel xanthan–glucomannan (XG). These two different systems can be considered as case systems representative of two types of hydrogels, i.e., chemical and physical gels.

2. The systems

Poly(vinyl alcohol) (PVA), is a biocompatible polymer already used in biomedicine. Its tendency to form physical gel by freeze–thaw cycles is known [9]. Chemical gels derived by networking PVA chains with low molecular weight cross-linkers are also known [10]. Here, we present, as case system, a new type of chemical hydrogel based only on PVA since the cross-linking agent is a derivatized PVA chains. These chains, called telechelic PVA, bear at each end a reactive group able to form a cross-link with hydroxyl moiety contained in PVA [7]. The cross-linking reaction allows to obtain a chemical PVA hydrogel without introducing any molecule chemically different from PVA and therefore preserving the biocompatibility of the starting material.
As second case system, we focused on a physical hydrogel obtained by the mixing of two different biopolymers. These gels, characterized by the simultaneous presence of two different polymer chains in their network, are often called “synergic”. In this system, the first polymer is a microbial polysaccharide named xanthan which has a cellulosic backbone chain. On every glucose ring, a side chain made of three saccharidic residues, bears charged groups which confer a polyelectrolytic behavior to the chain. The second polymer component of this synergic hydrogel is a linear polysaccharide of vegetal source, a glucomannan, made by alternating a glucose with a mannose residue. Hydrogen bond interactions are responsible for the network formation.

Both these polymer gels, being almost perfectly transparent, are good candidates for DLS studies. As it is usual for polymer hydrogels [11], both of them present a strong nonfluctuating component in the scattered light, so that after an initial decay the dynamic structure factor \( f(q, t) \) saturates at long time to a constant value \( f(q, \infty) \). The presence of this static background has been attributed to scattering from microscopic heterogeneities formed during the crosslinking process and/or dust [12,3] trapped into the gel. However, the observed saturation in the dynamic structure factor can also be explained by regarding the polymer gel as a nonergodic media [1], since the constraints due to the cross-links restricts the movement of fluctuating particles into a finite volume of the phase space. Although both these models explain the observed saturation of the dynamic structure factor, the dependence of this quantity on the wave vector \( q \) is different for the two models [3]. As we will see, for both polymers the data are described consistently with the model of nonergodic gel.

3. Light scattering from nonergodic gels

Most of the systems studied by DLS are ergodic. During the measurement time scale the system evolves through a representative fraction of the full ensemble of configurations and time-average of the scattered light intensity correlation function (ICF) is equal to its ensemble average. The ensemble averaged ICF may be interpreted directly in terms of ensemble-averaged properties of the medium through the Siegert relation:

\[
g^{(2)}(q, t) = \frac{\langle I(q, 0)I(q, t) \rangle}{\langle I(q, 0) \rangle^2} = 1 + |\beta f(q, t)|^2 ,
\]

where \( t \) denotes time, \( I(q, t) \) is the scattered intensity at the scattering vector \( q \), \( \beta \) is the coherence factor (\( \leq 1 \)) and \( f(q, t) \) is the dynamic structure factor. The angular brackets in Eq. (1) denotes an ensemble average but thanks to the ergodicity of the system one can replace it with a time average, the quantity directly obtained from a single DLS measurement.

In gel systems Eq. (1) does not help. The scatterers are in fact localized near fixed average positions and can only execute limited Brownian motions about these positions. This nonergodic system will be trapped in a restricted region of phase space, or subensemble. For this reason the time-averaged ICF, obtained in a single measurements, is not equal to the ICF averaged over a set of configurations representative of the full ensemble. Ad hoc procedures of collecting data have been adopted [1–3]
for evaluating the dynamic structure factor of nonergodic systems and in particular of polymer hydrogels.

A first procedure is due to Pusey and Van Megen [1,2], who calculated the scattering properties of a single scattering volume in the nonergodic medium and used this to obtain \( f(q,t) \) from a single ICF measurement. Indicating with \( \langle I(q) \rangle_E \) and \( \langle I(q) \rangle_T \) the total intensity of scattered light measured for the nonergodic system by averaging over the ensemble, and over the time, respectively, the ratio \( Y \) is defined as:

\[
Y = \frac{\langle I(q) \rangle_E}{\langle I(q) \rangle_T}.
\]  

(2)

The correct normalized dynamic structure factor is expressed by

\[
f(q,t) = \frac{Y - 1}{Y} + \frac{1}{Y} \left[ g^{(2)}_T - \sigma^{(2)}_1 \right]^{1/2},
\]

(3)

where \( \sigma^{(2)}_1 \) is the mean-square intensity fluctuation,

\[
\sigma^{(2)}_1 = \frac{\langle I(q)^2 \rangle_T}{\langle I(q) \rangle_T^2} - 1.
\]

(4)

In a second method, due to Xue et al. [3], the corrected ensemble averaged ICF is directly measured moving the sample in the incident laser beam so that different microscopic regions, i.e., different scattering volumes, are illuminated while collecting data. The intensity correlation function \( g^{(2)}(q,t) \) obtained following this procedure, correctly decays to zero for delay time \( \tau \) greater than a characteristic time \( \tau_2 \), given by the ratio between the beam diameter and the rotation velocity. In order to separate the characteristic ensemble averaged ICF of the network from the instrumental time scale corresponding to the sample rotation, one has to choose a proper rotation velocity. If the movement of the sample is slow enough the network characteristic time \( \tau_1 \) and the sample rotation time \( \tau_2 \) will be clearly separated, \( \tau_1 \ll \tau_2 \), and the ensemble averaged ICF can be easily obtained as the contribution at shorter times. The \( f(q,t) \) function is then directly obtained, as for ergodic systems, by means of the usual Siegert relation reported in Eq. (1).

By a comparison between the two methods it appears that the procedure of Xue et al. [3] is simpler and more robust but it needs a quite long time for measurements with a sufficiently slow rotation of the sample. However, the procedure of Pusey et al. [1,2] is quicker but it is based on the assumption that the intensity of scattered light is detected from an area less than a laser speckle size on the photon detector, i.e., the spatial coherence factor \( \beta \) is assumed equal to 1. If this approximation is not valid, the obtained \( f(q,t) \) is affected by an error of the order \( 1 - \beta^2 \) or less that can modify the overall shape of the \( f(q,t) \) in a way not easily predictable [1]. Moreover, the choice of the scattering volume from which data are collected is critical, because of the possible presence of dust [2].

In a previous paper [6] we have applied the Pusey and van Megen method [1,2] to the study of TPVA chemical hydrogel, here we used both approaches [1–3].
4. The model

As for any other static or dynamic factor, \( f(q,t) \) contains the dynamic and structural characteristic parameters of the network that has to be extracted by means of a suitable model.

Hydrogels are heterogeneous systems even in the ideal case of regularly spaced network chains [5]. Due to the intrinsic complexity of these systems, the calculation of the dynamical structure factor on the basis of a model that accounts for the details of the network structure and dynamics is a difficult task. However, in recent years several models, describing the complex structure of these gels in terms of a fractal structure made of basic units called “blobs”, have been proposed. We adopted the model of Krall et al. [4,5] for fractal gel dynamics. The model describes a nonergodic system in terms of a mechanically coupled set of “blobs”. Definition of this unit is on purpose rather loose and is related to the chemical details of the systems such as the functionality of the cross-links. On the other hand, an assembly of blobs is a convenient way to describe a system undergoing density fluctuation.

Because of the solid-like character of the gel, translational and rotational modes are frozen and the internal dynamics of the system are discussed in terms of \( N+1 \) successively imbedded subclusters. There is a hierarchy of sub-clusters enumerated by their radii \( R_i \) with \( i = 0, 1, \ldots, N \), where sub-cluster \( R_i \) is contained within sub-cluster \( R_{i+1} \). Sub-cluster 0 is the blob with \( R_0 = 1/q \) while sub-cluster \( N \) is the entire cluster with \( R_N = R_c \). These sub clusters are treated as independent over damped harmonic oscillators with spring constant \( k_i \) and relaxation times \( \tau_i \) linked by the relationship

\[
\tau_i = \frac{6\pi\eta R_i}{k_i}.
\] (5)

The blob mean squared displacement, \( \langle \Delta r^2(t) \rangle \), is the sum of all the oscillator contributions up to a cluster domain: \( \sum_{i=0}^{N} \langle \Delta r_i^2 \rangle \). According to the equipartition of energy principle, these satisfy \( k_i \langle \Delta r_i^2 \rangle = 3K_B T \), where \( K_B \) is the Boltzmann’s constant. Similarly, the full dynamic behavior of \( \langle \Delta r^2(t) \rangle \) is the sum of the time-dependent mean squared displacements

\[
\langle \Delta r_i^2(t) \rangle = \langle \Delta r_i^2 \rangle [1 - \exp(-t/\tau_i)],
\] (6)

carried by each sub-cluster. Passing from a discrete sum over the sub-clusters \( i = 0, 1, \ldots, N \) to an integration over their size \( R \), after a suitable approximation for the lower limit of the integral, Krall et al. [4,5] obtain the stretched exponential relationship:

\[
\langle \Delta r^2(t) \rangle = \frac{3K_B T}{\beta k_c \ln(f)} [1 - \exp(-t/b\tau_c)^p],
\] (7)

valid for a range of times up to \( 10\tau_c \). In this expression \( k_c \) is the spring constant of the oscillator representing the cluster, \( \tau_c = 6\pi\eta R_c/k_c \) is the time needed for the cluster to relax to the equilibrium position, \( \beta \) and \( p \) are characteristic parameters of the fractal properties of the network, \( b \) is equal to \( b = [\Gamma(1-p)]^{1/p} \), where \( \Gamma \) is the usual gamma function, and \( f \) is a fixed scale factor defined by \( f = R_{i+1}/R_i \). Inserting Eq. (7) in the
general expression of the $f(q,t)$

$$f(q,t) = \frac{S(q,t)}{S(q,0)} = \exp \left[ -q^2 \frac{\langle \Delta r^2(t) \rangle}{6} \right].$$

(8)

Krall et al. [4,5] obtain the following fitting expression:

$$f(q,t) = \exp [-(q\delta)^2[1 - \exp [-{(t/\delta)}^p]]],$$

(9)

from which it is possible to determine $\delta^2$, $\tau$ and $p$. The quantities $\delta^2$ and $\tau$ are defined from the previous expressions as $\delta^2 = K_B T/2k_c \ln(f)$ and $\tau = b\tau_c$.

5. Experimental section

Poly(vinyl alcohol) hydrogels were prepared as described in a previous paper [6] at polymer concentration of 10% (w/v).

Xanthan is a product from Kelco (USA). A controlled degradation was carried out by sonating the polysaccharide for 30 min by using a sonicator (Sonics and Materials, inc.) at full power equipped with macrotip in the presence of 5% (v/v) acetone as radical excavenger. After exhaustive dialysis against water, the polymer solution was brought to a concentration of 0.5% (w/v), determined by dry weight analysis. Number average molecular weight of this sample was $8 \times 10^5$ g/mol, determined by membrane osmometry.

Glucomannan from Konjac was a FMC product. The polysaccharide was dispersed in water by stirring overnight and then autoclaved for 20 min at 120°C. The stock solution with a polymer concentration of 0.5% w/v determined by dry weight analysis, was kept at 4°C.

The molar ratio of glucose/mannose residues in the glucomannan chain, determined by $^{13}$C NMR, was equal to 0.6, in agreement with the literature [13]. Phase diagrams at different temperatures and compositions were obtained by the “falling beads” method.

Water with MilliQ purity was used throughout the experiments.

Dynamic light scattering set up consisted of a 5 mW He-Ne laser source with a vat cell mounted on a goniometer plate and equipped with an optical fiber connecting the photon collection optics to the photomultiplier (Hamamatsu, Japan). Correlator (BI - 9000AT) and software from Brookhaven Instruments (USA) were used with an array of 400 logarithmically spaced channels for data storage and processing. DLS measurements for the xanthan/ glucomannan physical gels were carried out at weight fractions, $w_x$, equal to 0.3 and 0.5. For the latter sample measurements were carried out by both methods previously described [1–3].

For the TPVA samples, due to evolution of the gelling process, only the Pusey method [1,2] was used as a shorter time for the measurements.
6. Results and discussion

6.1. Telechelic PVA chemical hydrogels

The gelation process for this system was carried out in situ during data collection. The system reached the percolation threshold, evidenced by an abrupt decreasing of the \( g_T^{(3)}(q,0) \), after about 100 min at the conditions described by Barretta et al. [6]. Already at the early stages, after crossing the gel point, the system showed a marked nonergodic behavior. The obtained dynamic structure factor was analyzed in term of the fractal gel model of Krall et al. [4,5]. In Fig. 1 the \( f(q,t) \) at 60\(^\circ\), 70\(^\circ\) and 80\(^\circ\) fitted with this model are shown. In this study a \( \delta \) value of 24 ± 2 nm was obtained, consistent with the results obtained by compression modulus and equilibrium swelling measurements on similar PVA networks [7,8]. Values of \( \tau \) and \( p \), respectively, equal to 300 and 0.8 \( \mu \)s are also obtained within ±10%.

The behavior of the \( f(q,t) \) reported in Fig. 1 gives a clear indication of the non-ergodic nature of the TPVA gels. In fact, according to Xue et al. [3], the nonergodic behavior of a gel is characterized by the dependence of \( f(q,\infty) \) on the scattering vector \( q \), while the correlation times do not change as a function of \( q \).

6.2. Synergic physical hydrogel

The phase diagram reported in Fig. 2 shows the dependence of the melting temperature of the gel on the weight fraction of xanthan, \( w_x \). The system is in a stable gel phase for \( w_x \) between about 0.3–0.7 and up to a temperature of 48\(^\circ\)C.

![Fig. 1. Dynamic structure factor, \( f(q,t) \), for TPVA sample obtained at 60\(^\circ\) (○), 70\(^\circ\) (□) and 80\(^\circ\) (△). Full lines are the fits according to Eq. (9).](image-url)
Physical gels like the xanthan/glucmannan systems are suitable for a study of the ICF according to the method of Xue et al. [3] as this type of gel does not evolve during the time needed for measuring the $g_r^{(2)}(q,t)$ at slow rotation velocity.

It is worth to note that a comparison of the $f(q,t)$ functions, shown in Fig. 3, obtained on the same gel with both methods of Pusey [1,2] and Xue [3], indicates a very good agreement between the two methods.

The dependence of the $f(q,t)$ from the scattering vector values was studied for the system with composition $w_x=0.3$ and the dynamic structure factors obtained at $70^\circ$, $80^\circ$, $90^\circ$ and $100^\circ$ are reported in Fig. 4. As for the TPVA chemical gels, the $f(q,\infty)$ values as well as the correlation times, $\tau$, show a behavior typical of nonergodic systems. Also, in this case the model proposed by Krall et al. [4,5] was used and the fits are shown in Fig. 4. The model permits to obtain values $p, \delta$ and $\tau$ of, respectively, $0.9 \pm 0.2$, $28 \pm 2$ nm and $180 \pm 40$ $\mu$s.

7. Concluding remarks

Both the chemical and physical hydrogels investigated in this study behave as nonergodic systems. Although Krall model [4,5] is devised for colloidal systems, we applied this model to our hydrogels. The values of average mesh dimension and correlation times obtained from this analysis are in reasonable agreement with the typical values found for similar gels. The values of $\delta$ and $\tau$ show that in these systems the polymer chains form a nanostructured network, referring to the average dimension of the meshes, and that the time scale of the chains dynamics is of few hundreds of
Fig. 3. Dynamic structure factor, $f(q,t)$, for the physical gel with $w_ε = 0.5$ as obtained with the methods of Pusey [1,2] (□) and Xue [3] (●).

Fig. 4. Dynamic structure factor, $f(q,t)$, for the physical gel with $w_ε = 0.3$ at $70^°$ (∆), $80^°$ (◇), $90^°$ (○) and $100^°$ (□). Full lines are the fits according to Eq. (9).

microseconds. This confirms that, despite the presence of about 99.5% (w/v) of water, a quite rigid polymer network is present in the hydrogel. Further investigations are under way to achieve a better knowledge of the behavior of this system as a function of parameters as hydrogel composition and temperature.
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