Swelling and viscoelastic properties of new magnesium- acrylate hydrogels

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ABSTRACT

In this paper we report on the preparation of a novel poly(magnesium acrylate) hydrogel (PAMGA) by free radical homopolymerization of magnesium acrylate in aqueous solution. The effect of the concentration of monomer and initiator on the rheological and swelling properties of PAMGA hydrogels was studied. In the equilibrium of swelling these hydrogels show a phase transition characterized by the transformation from a transparent to an opaque-milky structure associated with a change in the viscoelastic properties of the hydrogels. The influence of the concentrations of monomer and initiator on the phase transition has been studied and the results show that the temperature of the phase transition increases with both the concentration of monomer and the concentration of initiator, being the effect of the initiator more pronounced.

INTRODUCTION

Hydrogels are nowadays the focus of intensive investigations in biomedical and biotechnological areas of research due to their biocompatibility [1-6]. Hydrogels are formed by hydrophilic polymer networks that are capable of swelling up to 1000 times their volume in aqueous solution. The degree of swelling is controlled by the energy changes associated with i) the mixing of polymer and water molecules that increases the entropy of the system by forming hydrogen and dipole bonds with the water and tends to increase the gel volume, and ii) the network elasticity of the hydrogels when the volume increases, which acts to counteract the volume expansion [7]. Furthermore, the degree of swelling depends strongly on the environmental conditions such as pH, temperature or ionic strength. Thus, by changing these parameters it is possible to induce a reversible volume phase transition by swelling or collapsing the polymer network [7-8]. This property has been used to prepare smart materials capable to respond to different stimuli and permits to obtain polymer matrices for application in sensors, artificial muscles or drug delivery systems [9-12].

Temperature is the physical stimuli mostly used to produce volume phase transitions. For most polymeric materials, an increase in temperature results in an increase of the polymer solubility. This behavior contrasts with the effect observed in poly(N-isopropyl-acrylamide) (PNIPAM) that exhibits a lower critical solubility temperature (LCST) [13]. The volume transition is associated with the decreasing solvency of water for PNIPAM as temperature increases. The polymer network collapses as a result of the magnification of the polymer hydrophobic character and the ejection of water from inside the network to the

surrounding medium. In other cases the external stimuli provoke a variation in the color, conductivity or rheological behavior of the hydrogel that is interesting not only for its applications but also from a theoretical point of view [14-16].

Polymer hydrogels based on polyacrylates have received much attention for its applications as thickening agents, super-absorbent gels, electrophoresis applications and so forth. Some of these polyacrylates and their salt forms have been extensively studied from the point of view of their structure, properties and applications [17-22]. However, most of these studies focus on the use of a two-step process to obtain the hydrogels from preformed polymer chains that are neutralized with the desired cation [23]. In this sense, recently a new acrylate polymer, poly(magnesium acrylate), synthesized from magnesium acrylate monomer in a one-step process, has been recently prepared in our lab [24,25].

In previous papers [24,25] we reported on the synthesis of the new monomer, magnesium acrylate monomer, and its polymerization to render a biocompatible hydrogel, and the characterization of the gel properties. One of the outcomes of the previous paper [25] was the observation of an optical transition from transparent to a milky appearance between 12 and 15 °C. The objective of the present paper is to go deeper in the understanding of this transition through the study of the viscoelastic behavior of the hydrogels.

EXPERIMENTAL PART

Materials

Acrylic acid monomer, magnesium hydroxide and the initiator ammonium persulfate were purchased from Sigma and used without further purification.

Sample preparation

Magnesium acrylate monomer (AMGA) was synthesized by a neutralization reaction between acrylic acid and magnesium hydroxide described elsewhere [24,25]. PAMGA hydrogels were obtained through free radical homo-polymerization [24,25]. A set of samples was prepared to study the influence of monomer and initiator concentration on the swelling and viscoelastic properties of the hydrogels. Monomer concentration was varied between 20 and 40 % (w/w) and initiator concentration was varied between 10 and 40 mM. The appropriate amounts of ammonium persulfate (initiator) and magnesium acrylate (monomer) were dissolved in 40 mL of water. Solutions were poured out into Petri dishes and allowed to react at 60 °C for 5 min. When the acrylate monomer began to polymerize (an increase in temperature was observed), the reaction was slowed down by placing the reactor in a thermostatic bath at 10 °C for 5 hours until the polymerization was completed.

Swelling measurements

Specimens of 2 cm in diameter and around 0.2 cm in thickness were cut off from the fresh prepared hydrogel samples (relaxed state). Each specimen was weighted (m_0) and introduced in an excess of water. At increasing times,

the specimen was extracted from water, the excess of water eliminated, and weighted (m_t) until equilibrium is achieved. The swelling degree from the relaxed state was calculated at different times with: $(m_t - m_o)/m_o$. Average values were obtained from three specimens.

Viscoelastic measurements

Dynamic viscoelastic measurements were performed in a TA Instruments AR1000 Rheometer using the parallel plate (2 cm) shear mode to measure the storage modulus, G' , the loss modulus, G'' , and the loss tangent, $\tan \delta$. To prevent the influence of aging and the kinetics of gelation on the G' modulus, measurements were performed 24 h after the gels were prepared (initial gels). Three specimens of each sample (2 cm in diameter and around 0.2 cm in thickness) were analyzed to obtain average values. The linear viscoelastic region was located with the aid of a torque sweep. Frequency scans from 1 to 100 Hz in isothermal conditions and torque 50 μNm were carried out. Temperature sweeps between 10 and 100 $^{\circ}\text{C}$ at scanning rates of 10 and -10 $^{\circ}\text{C}/\text{min}$, frequency 1 Hz, and torque 50 μNm were also carried out. To avoid the evaporation of solvent in the course of the rheological measurements a solvent trap from TA Instruments was used.

RESULTS AND DISCUSION

The effect of monomer concentration and initiator concentration on the swelling properties of PAMGA hydrogels was studied and the results are represented in Figure 1a and 1b, respectively. The kinetics of swelling are similar for all the systems studied and the equilibrium of swelling is reached after approximately 1-2 days. The degree of swelling in the equilibrium (calculated from the relaxed state) increases with monomer concentration as can be observed in Figure 1a. This behavior indicates that samples prepared at higher monomer concentrations are farther from the equilibrium state than the lower concentrated samples. In Figure 1b the effect of initiator concentration on the swelling kinetics is depicted. An increase in the initiator concentration produces an increase in the equilibrium of swelling from the relaxed state. In this case, the effect must be interpreted on the basis of structural aspects since the monomer concentration is the same for all the samples. Probably, a more opened structure with a higher number of defects (free-end chains, for example) may account for the increase of swelling with the initiator concentration.

PAMGA hydrogels swelled to equilibrium were characterized for their viscoelastic properties. To determine the linear viscoelastic region (LVR) a torque sweep was carried out. Figure 2 shows the variation of the elastic and the loss modulus as a function of the applied torque at 1Hz and 20 °C for an PAMGA hydrogel of concentration 30 %(g/g) and initiator concentration 10mM. As can be observed, the LVR spreads over a wide range of torque from 1 to 100 μ Nm. A constant torque of 50 μ Nm, within the LVR, was selected to carry out all the viscoelastic measurements.

Figure 3 shows the frequency sweeps corresponding to samples prepared from different monomer and initiator concentrations. In both figures we can observe that the storage modulus at low frequencies is approximately independent of frequency and presents a finite value at zero frequency. This behavior is characteristic of solid-like systems, as corresponds to chemical gels made up of permanent cross-links. Figure 3a depicts the effect of monomer concentration on the evolution of the storage modulus and the loss modulus as a function of frequency. In this figure we can observe the following features: i) the storage modulus increases with monomer concentration indicating an increase in the cross-linking density and ii) the independence of the storage modulus with frequency is more pronounced as the monomer concentration increases. In Figure 3b the effect of the initiator concentration is depicted. We can observe both, a decrease in the storage modulus as the initiator concentration increases and the loss of the independence of the storage modulus with frequency at low frequencies. These results can be interpreted considering that an increase of initiator concentration produces an increase in the network defects that include free chain-ends or elastically ineffective chains.

The effect of temperature on the viscoelastic properties of PAMGA gels was also investigated. In Figure 4 G' is depicted as a function of frequency for a PAMGA hydrogel (monomer concentration 30 % (w/w) and initiator concentration 10 mM). Experiments were carried out at four different temperatures between 10 and 80 °C. As can be observed, the curves for temperatures 10, 20 and 30 °C are rather superposable. The curve corresponding to 80 °C present the same behavior but higher G' values. These observations seem to be consistent with a transition from an independent

temperature behavior to a dependent temperature behavior that takes place between 30 and 80 °C. To confirm this result, temperature sweeps for different PAMGA gel samples were performed.

Figures 5a and 5b show the evolution of the storage modulus with temperature for PAMGA hydrogels prepared from different monomer and initiator concentrations. For all the samples, except for sample prepared with an initiator concentration of 40 mM, the behavior is virtually the same. At low temperatures a pseudo-equilibrium modulus exists (storage modulus independent of temperature). At a certain temperature, a transition takes place in which the storage modulus increases with temperature, and finally, the storage modulus levels off to a new pseudo-equilibrium modulus. These observations confirm the results obtained in Figure 4. The temperature at which the transition takes place increases with both, monomer and initiator concentrations; although the effect of the initiator concentration is more conspicuous: the variation is erratic and for concentrations higher than 40 mM the shape of the curves changes dramatically. There is not an initial pseudo-equilibrium plateau at low temperatures but a decrease of the storage modulus with temperature. This behavior is characteristic of weak gels made up of non-permanent cross-links, of physical rather than chemical nature, that weaken with temperature, and may be due to an increasing number of network defects (chain loops, free-chain ends, etc.). Nevertheless, this system also shows a transition at high temperatures in which the storage modulus sharply increases with temperature.

The transition occurring at high temperatures implies an increase in the elastic modulus of the PAMGA gels due to an increasing compactness of the

gel structure and it is probably related to a volume phase transition. The shift from hydrophilic to hydrophobic interactions may account for this behavior that has also been observed by other experimental techniques [24,25].

To demonstrate that hydrophobic interactions rather than chemical or permanent modifications were responsible for the transition in PAMGA gels a study of the thermoreversibility of the transition was performed.

Figure 6 shows three consecutive temperature scans between 10 and 100 °C for a PAMGA hydrogel: heating from 10 to 100 °C, cooling from 100 to 10°C and reheating from 10 to 100 °C. The evolution of the storage modulus as a function of temperature for the three steps is depicted. A transition at around 50 °C can be observed for the first and the second step, demonstrating the reversibility of the process. In the third step the transition, within the experimental uncertainties, is shifted to around 65 °C probably due to molecular reorganizations taking place as a consequence of the previous steps.

CONCLUSIONS

PAMGA hydrogels can be obtained by free radical homopolymerization of magnesium acrylate monomer in aqueous solutions. The hydrogels obtained do swell in water until equilibrium is reached. PAMGA hydrogels swelled to equilibrium show a viscoelastic behavior characteristic of chemical gels made up of permanent cross-links. The elastic modulus of the hydrogels can be controlled both, through the control of the monomer concentration and the initiator concentration. The concentration of monomer increases both, the cross-linking density and the elastic properties of the hydrogels, whereas the initiator

concentration increases the defects of the network, that include free chain-ends or elastically ineffective chains. In the equilibrium of swelling PAMGA hydrogels show a phase transition characterized by the transformation from a transparent to an opaque-milky structure. This phase transition can be observed by viscoelastic measurements through a change of slope in the representation of the elastic modulus as a function of temperature. The transition is probably related to a shift from a state where hydrophilic interactions predominate to a state where the hydrophobic interactions prevail.

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FIGURE CAPTIONS

Figure 1.- Swelling kinetics of PAMGA hydrogels at 20 °C as a function of a) monomer concentration: (■) 20; (●) 30 and (▲) 40% (w/w) and b) initiator concentration: (■) 10 mM; (●) 15 mM; (▲) 20 mM and (▼) 40 mM.

Figure 2.- Storage modulus (●) and loss modulus (▲) as a function of the oscillation torque at 1Hz and 20 °C for a PAMGA hydrogel of monomer concentration 30% (w/w) and initiator concentration 10 mM. Determination of the Linear Viscoelastic Region (LVR).

Figure 3.- Storage modulus (full symbols) and loss modulus (empty symbols) as a function of oscillation frequency at 20 °C. a) Effect of the monomer concentration: (■) 20; (●) 30 and (▲) 40% (w/w) (initiator concentration 10mM) and b) Effect of the initiator concentration: (■) 10 mM; (●) 15 mM; (▲) 20 mM and (◆) 40 mM (monomer concentration 30% (w/w)).

Figure 4.- Storage modulus as a function of oscillation frequency for PAMGA hydrogels of monomer concentration 30 % (w/w) and initiator concentration 10 mM. Experiments carried out at different temperatures: (■) 10; (●) 20; (▲) 30 and (▼) 80 °C

Figure 5.- Storage modulus at an oscillation frequency of 1 Hz as a function of temperature for PAMGA hydrogels. a) Effect of monomer concentration: (■) 20; (●) 30 and (▲) 40% (w/w) (initiator concentration 10mM) and b) Effect of

initiator concentration: (■) 10 mM; (●) 15 mM; (▲) 20 mM and (◆) 40 mM(monomer concentration 30% (w/w).

Figure 6.- Storage modulus as a function of temperature. Consecutive temperature sweeps between 10 and 100 °C: (■) curve obtained by heating from 10 to 100 °C at a heating rate of 10 °C/min; (●) curve obtained by cooling from 100 to 10 °C at a cooling rate of -10 °C/min and (▲) curve obtained by heating again from 10 to 100 °C at 10 °C/min. PAMGA hydrogels of monomer concentration 30 % (w/w) and initiator concentration 10 mM. Oscillation frequency 1Hz.