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Equilibrium swelling and mechanical properties of hydrogels of acrylamide and itaconic acid or its esters

E. Vallés[1], D. Durando[1], I. Katime[2], E. Mendizábal[3], J. E. Puig[3,*]

[1] Planta Piloto en Ingeniería Química, Bahía Blanca 8000, Argentina
[2] Grupo de Nuevos Materiales, Departamento de Química Física, Universidad del País Vasco - Campus Leioa, 48080 Bilbao, España
[3] Departamentos de Química y de Ingeniería Quimica, Universidad de Guadalajara, Boul. M. Garcia Barragán # 1455, Guadalajara, Jal. 44430, Mexico

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Summary

The equilibrium swelling and the plateau elastic modulus of a family of hydrogels made by the polymerization of acrylamide with itaconic acid or some of its esters were investigated as a function of composition and crosslinking degree to find materials with satisfactory swelling and elastic properties. We show that an appropriate selection of the comonomers and the concentration of the crosslinking agent is very important to produce hydrogels with large swelling capacity and good mechanical attributes. Tailoring of mechanical properties and swelling can also be achieved by this method.

Introduction

Hydrogels are chemically or physically crosslinked polymers that can absorb large amounts of water without dissolving and without loosing their shapes (1, 2). For many applications, the combination of large swelling and good mechanical properties is important (2-9). Usually, large swelling is accompanied by poor mechanical properties. There are several alternatives to find a compromise between "large swelling" and "good mechanical behavior". One is by varying the nature and the crosslinking degree of the hydrogels. Increasing the crosslinking density usually improves the elastic modulus and the structural properties but it decreases the water absorption capacity (10). Other is by polymerizing hydrophilic monomers, which favor swelling, with hydrophobic ones, which enhance the mechanical properties (11). Another one is by varying the polymerization conditions (12).

Here we report the maximum degree of swelling or equilibrium swelling and the plateau elastic modulus of a family of hydrogels of acrylamide copolymerized with itaconic acid or its monoesters as a function of composition and crosslinking degree. We show that large swelling can go "hand-to-hand" with good mechanical properties provided that the right combination of hydrophilic and hydrophobic monomers and crosslinking degree is used.

Experimental Section

Acrylamide and itaconic acid (IA) were 99% pure from Aldrich and were used without further purification. The monoesters [methyl, 2-ethoxyethyl, 2,2-(ethoxyethoxy)ethyl and 2, 2-(ethoxybutoxy)ethyl monoitaconates] were synthesized by the reaction of IA with an excess of the corresponding alcohol (99% pure from Aldrich) in the presence of acetyl chloride (Merck) and isolated as described elsewhere (13).

Hydrogels were prepared by dissolving 10 parts by weight of the corresponding amounts of acrylamide and IA or one of its monoitaconates in 90 parts by weight of water together with the crosslinking agent (NMBA). The solution was loaded in a test tube, sparged with argon and heated to 60 °C. Then the reaction was carried out for 3 hours using potassium persulfate (1 wt% with respect to monomers). For hydrogels made with the higher monoitaconate concentrations, up to 7 hours of reaction were needed to produce the gel. Once the reaction was over, each test tube was broken and the hydrogels were immersed in water to eliminate unreacted monomers. Then the hydrogels were dried at room temperature and cut in the shape of disks (10 mm in diameter and 1 mm in thickness). These disks were sanded and polished to

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[*] Corresponding author

produce two parallel faces. This procedure was necessary to obtain suitable samples to put in the parallel plates of the rheometer after re-swelling for viscoelastic measurements. To avoid the deformation and rupture of the disks during swelling, they were put in a dessicator jar containing water in the bottom to humidify slowly the samples; then, water was added dropwise to the disks and finally they were immersed in water until their equilibrium swelling (Sw_∞) was attained. Sw_∞ is defined here as:

$$Sw_\infty = \frac{w_\infty - w_0}{w_0} x\,100 \qquad (1)$$

where w_o is the weight of the xerogel and w_∞ is the weight of the hydrogel at equilibrium swelling, i.e., after a long period of swelling. Sw_∞ was estimated by fitting the swelling versus time data to a second order kinetic equation of the form (14):

$$\frac{t}{Sw(t)} = \frac{1}{Sw_\infty} t + \frac{1}{k_{sw} Sw_\infty^2} \qquad (2)$$

where $Sw(t)$ is the swelling at time t and k_{sw} is a second order swelling rate constant.

Strain and frequency sweeps were performed on hydrogel disks swollen up to equilibrium conditions in a Rheometrics RDS-II mechanical spectrometer and parallel plates geometry (25 mm in diameter). Measurements were performed at room temperature. To prevent water evaporation during measurements, a humidification chamber containing wetted sponges was placed around the parallel plates fixture. Also, to avoid slippage and to have better adhesion between the hydrogel and the plates, a fine sandpaper was glued to both plates.

Results and Discussion

Figure 1 shows plots of *t/Sw* versus time for the swelling kinetics of hydrogels made with acrylamide and methyl monoitaconate as a function of monoitaconate content. The predictions of the second order kinetic equation (eq. 2), shown as solid lines in this Figure, follow quite well the experimental data for all compositions. Similar plots were obtained with the other hydrogels, demonstrating that the swelling of these hydrogels indeed obeys a second order swelling kinetic equation From the slope of these plots, the value of Sw_∞ can be obtained.

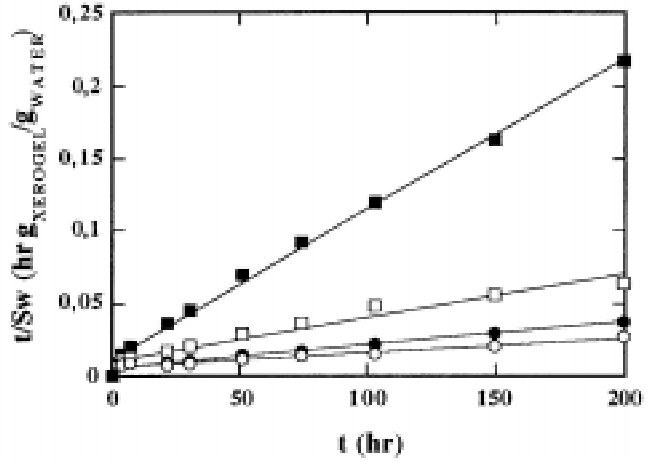

Figure 1. Swelling kinetic data for hydrogels of acrylamide/methyl monoitaconate represented according to eq. (2) as a function of mol fraction of methyl monoitaconate: (■) 0; (□) 0.08; (l) 0.174; (m) 0.287. Solid lines represent the best fit of eq. (2).

Figure 2 and 3 show the equilibrium swelling, Sw_∞, versus comonomer (itaconic acid or the corresponding monoitaconate) concentration in the hydrogels made with 1 and 2 wt% NMBA, respectively. In general, Sw_∞ increases as the comonomer concentration augments. The largest swelling is achieved with the 2, 2 (ethoxybutoxy)ethyl monoitaconate – near 32,000 % at 0.072 mol fraction of comonomer, which is about 34 times larger than the swelling of the polyacrylamide hydrogel (917 %).

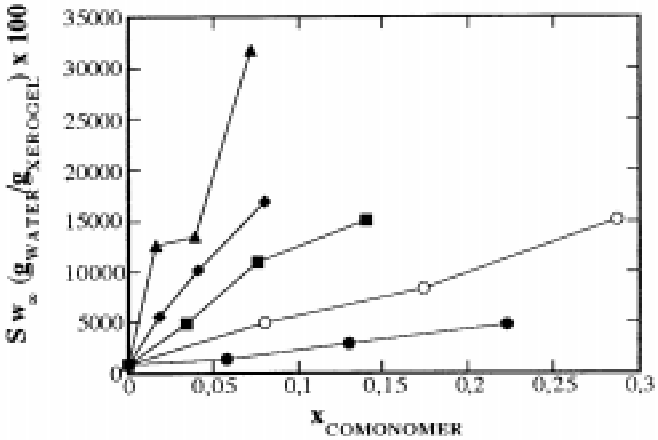

Figure 2. Equilibrium swelling versus comonomer content in the hydrogels made with 1 wt% NMBA: (■) itaconic acid; (○) methyl monoitaconate; (●) 2-ethoxyethyl monoitaconate; (◆) 2, 2 (ethoxyethoxy)ethyl monoitaconate; (▲) 2, 2 (ethoxybutoxy)ethyl monoitaconate.

It is interesting that the hydrogels made with the more hydrophilic comonomer, itaconic acid, swell less than those made with the 2, 2 (ethoxyethoxy)ethyl and 2, 2 (ethoxybutoxy)ethyl monoitaconates (Fig. 2), probably because the presence of the two ether groups in the structure of these hydrogels favors interactions with water molecules, which enhance the swelling. Also is remarkable that quite small concentrations of the more hydrophilic comonomers are required to increase substantially the water absorption capacity of the hydrogels.

The same trends observed in Figure 2 are depicted in Figure 3, i.e., Sw_∞ increases as the monoitaconate concentration augments; again, the hydrogels made with 2, 2 (ethoxybutoxy) ethyl monoitaconate exhibit larger swelling than the other hydrogels whereas those made with 2 (ethoxy)ethyl monoitaconate show the smallest water absorption capacity. Also, as expected, the degree of swelling decreases as the concentration of the crosslinking agent is increased (cf. Figs. 2 and 3)

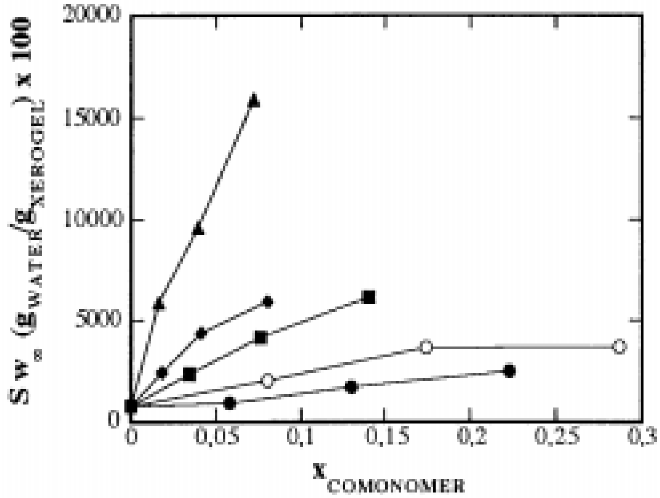

Figure 3. Equilibrium swelling versus comonomer content in the hydrogels made with 2 wt% NMBA: (■) itaconic acid; (○) methyl monoitaconate; (●) 2-ethoxyethyl monoitaconate; (◆) 2, 2 (ethoxyethoxy)ethyl monoitaconate; (▲) 2, 2 (ethoxybutoxy)ethyl monoitaconate.

Figure 4 shows a typical frequency sweep performed in the linear viscoelastic regime. The linear viscoelastic regime, defined here as the region where the elastic (*G'*) and the loss (*G"*) moduli are independent of strain amplitude, were determined for each hydrogel by performing a strain amplitude sweep at fixed frequency (1, 10 and 100 s^{-1}). From this Figure it is evident that *G'* > *G"* over the whole frequency range examined. The elastic modulus is constant and independent of frequency. This behavior is typical of ideal elastic networks (15). The loss modulus is also nearly constant up to frequencies close to 100 s^{-1}, but it increases considerably at higher frequencies. Also, as expected, the elastic modulus increases with the crosslinking degree. The frequency independence of *G'* allows to identify its measured value with that of the equilibrium elastic modulus, *G* (15).

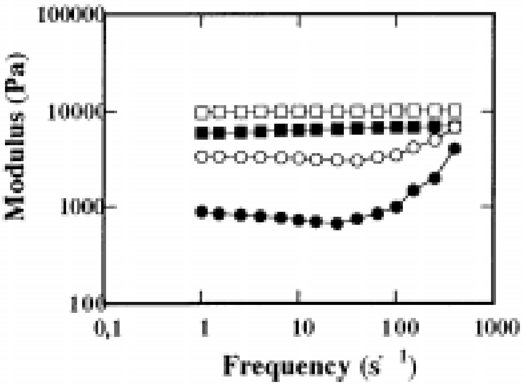

Figure 4. Elastic (□; ■) and loss (○; ●) modulus of a hydrogel of acrylamide and 2, 2-(ethoxyethoxy)ethyl monoitaconate (0.041 mol fraction) as a function of the degree of crosslinking: (open symbols) 2 wt% NMBA; (closed symbols) 1 wt% NMBA.

The elastic modulus (*G*) as a function of comonomer content is depicted in Figure 5 for the hydrogels made with 1 wt% NMBA. In general for this series, *G* decreases as the comonomer content in the hydrogels augments. This means that *G* drops as Sw_∞ increases, i.e., as the water content increases (cf. Figs. 2 and 5). This is because water virtually does not contribute to the mechanical properties. The 2, 2 (ethoxybutoxy) monoitaconate/acrylamide hydrogels exhibit the largest swelling (Fig. 2) and the lowest elastic moduli (Fig. 5). Moreover, hydrogels with similar degree of swelling have similar elastic modulus with the exception of those made with itaconic acid that have larger modulus. Inasmuch as the hydrogels were synthesized with identical concentrations of crosslinking agent and since the elastic modulus is directly proportional to the number density of crosslinks (15), it appears that the effective crosslinking density is about the same for all hydrogels, even though they may have different crosslinking efficiencies. The larger elastic modulus of the IA/acrylamide hydrogels may be due to the hydrogen bonding capacity of the IA which may increase the effective crosslinking density in the swollen state.

Figure 6 depicts the plateau modulus as a function of composition for the hydrogels made with 2 wt% NMBA. As expected form the arguments given above, G increases with the degree of crosslinking (cf. Figs. 5 and 6). Also, G is larger for all the hydrogels at equal composition, because of their smaller degree of swelling (cf. Figs. 2 and 3). Again, the 2,2-(ethoxybutoxy)ethyl monoitaconate hydrogels show the largest equilibrium swelling (Fig. 2) and the smallest modulus (Fig. 6). Also, the hydrogels made with IA and 2, 2 (ethoxyethoxy)ethyl monoitaconate exhibit the larger moduli, even larger than that of the polyacrylamide hydrogel (Fig. 6). Inasmuch as the hydrogels of IA and 2, 2 (ethoxyethoxy)ethyl monoitaconate swell about the same (Figs. 2 and 3), it is clear that the larger moduli exhibited by the IA hydrogels may be a consequence of its larger capacity of forming hydrogen bonds. On the other hand, both types of hydrogels are candidates for applications that require hydrogels with large swelling capacity and large plateau moduli.

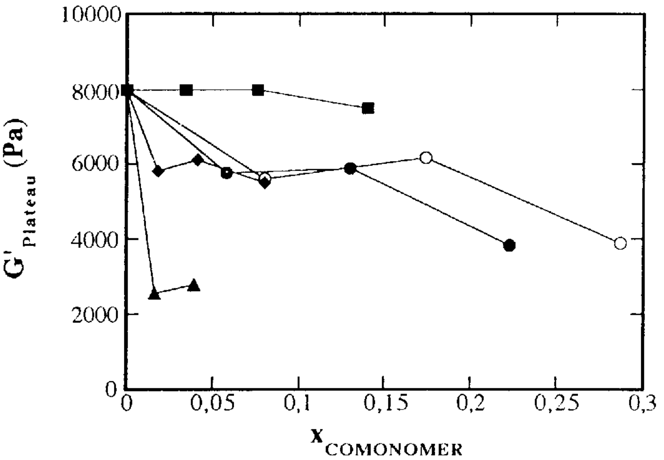

Figure 5. Elastic modulus versus comonomer content in the hydrogels made with 1 wt% NMBA: (■) itaconic acid; (○) methyl monoitaconate; (●) 2-ethoxyethyl monoitaconate; (◆) 2, 2 (ethoxyethoxy)ethyl monoitaconate; (▲) 2, 2 (ethoxybutoxy)ethyl monoitaconate.

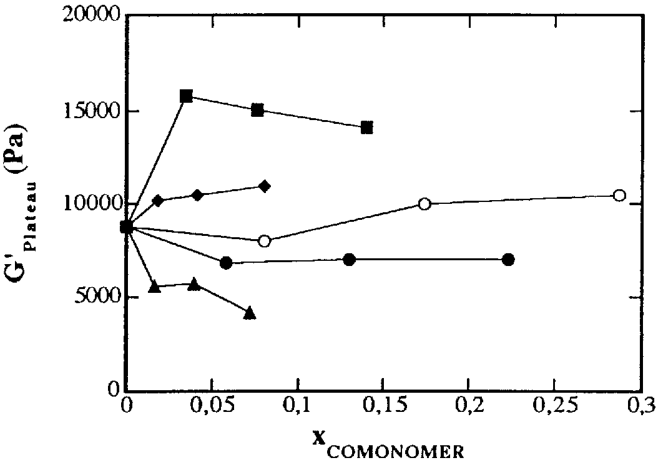

Figure 6. Elastic plateau modulus versus comonomer content in the hydrogels made with 2 wt% NMBA: (■) itaconic acid; (○) methyl monoitaconate; (●) 2-ethoxyethyl monoitaconate; (◆) 2, 2 (ethoxyethoxy)ethyl monoitaconate; (▲) 2, 2 (ethoxybutoxy)ethyl monoitaconate.

Conclusions

The degree of swelling and the mechanical properties of a family of hydrogels of acrylamide and itaconic acid or some of its monoitaconates are reported here. The degree of swelling and the elastic modulus can be tuned by varying the amount and type of comonomer as well as the degree of crosslinking. The swelling of the hydrogels follow a second-order kinetic equation. Hydrogels of IA and acrylamide exhibit an excellent combination of swelling degree and mechanical properties, but they are prone to pH and salt effects. This issue will be reported in a future publication.

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