Colloid Polym Sci 279: 323–330 (2001)

ORIGINAL CONTRIBUTION

M. Monleón Pradas
J. L. Gómez Ribelles
A. Serrano Aroca
G. Gallego Ferrer
J. Suay Antón
P. Pissis

Interaction between water and polymer chains in poly(hydroxyethyl acrylate) hydrogels

Received: 11 November 1999
Accepted: 28 July 2000

M. Monleón Pradas
J. L. Gómez Ribelles (✉)
A. Serrano Aroca · G. Gallego Ferrer
Center for Biomaterials
Universidad Politécnica de Valencia
Camino de Vera s/n
46071 Valencia, Spain

J. Suay Antón
Deptartment of Technology
'Jaume I' University
12071 Castellón, Spain

P. Pissis
Deptartment of Physics
National Technical University of Athens
Zografou Campus, 15780 Athens, Greece

Abstract Polymer networks of different cross-linking densities were prepared by copolymerisation of hydroxyethyl acrylate and ethylene glycol dimethacrylate. The average molecular weight between cross-links as well as the polymer chain mobility were characterised by means of dynamic–mechanical spectroscopy. Equilibrium sorption isotherms and the water uptake in immersion in liquid water allowed the determination of the Flory–Huggins interaction parameter between water molecules and polymer chain segments, which decreased with the water activity in the hydrogel and increased with the cross-linking density as a consequence of the hydrophobic character of the cross-linking agent. Dynamic sorption and desorption experiments were used to determine the diffusion coefficient.

Key words Hydrogels · Water sorption · Diffusion · Poly(hydroxyethyl acrylate) · Dynamic–mechanical properties

Introduction

Polymer hydrogels are hydrophilic polymer networks, able to absorb large amounts of water but insoluble in water because of the chemical or physical cross-links between the polymer chains. The good biocompatibility and water permeation properties and the possibility of synthesising materials with a broad spectrum of micromorphologies and specific properties have allowed polymer hydrogels to be used in many biomedical applications [1, 2].

The ability of a polymer network to absorb water depends for small network expansions mainly on the specific interaction between water molecules and polymer chains. According to the Flory–Huggins solution theory [3] the free energy of mixing polymer chains and water molecules is

$$\Delta G_{\mathrm{m}} = kT[n_{\mathrm{w}} \ln \phi_{\mathrm{w}} + \ln(1-\phi_{\mathrm{w}}) + \chi n_{\mathrm{w}}(1-\phi_{\mathrm{w}})] \ , \quad (1)$$

where χ is the water–polymer interaction parameter and n_{w} and ϕ_{w} are the number of water molecules and the volume fraction of water in the hydrogel respectively. The interaction parameter χ characterises the interaction between water molecules and polymer segments and takes higher values with increasing hydrophobicity of the polymer network.

From Eq. (1) an expression for the chemical potential of water mixed with the polymer network, $\hat{\mu}_{\mathrm{w}}^{\mathrm{hydrogel}}$, can be deduced. When a hydrogel is kept in an environment consisting of a vapour phase containing water, the thermodynamic equilibrium requires that

$$\hat{\mu}_{\mathrm{w}}^{\mathrm{hydrogel}} = \hat{\mu}_{\mathrm{w}}^{\mathrm{v}} \ , \quad (2)$$

with $\hat{\mu}_{\mathrm{w}}^{\mathrm{v}}$ the chemical potential of water in the vapour phase. From Eq. (2) it can be deduced that the activity of water in the swollen network, a_{w}, equals approximately the relative humidity (RH) of the vapour phase, which thus becomes a controllable parameter, and from Eq. (1) it follows that

$$\ln a_{\mathrm{w}} = \ln \phi_{\mathrm{w}} + (1-\phi_{\mathrm{w}}) + \bar{\chi}(1-\phi_{\mathrm{w}})^2 \ , \quad (3)$$

where $\bar{\chi}$, which is closely related to χ and coincides with it when χ is independent of composition [4], can be called an apparent interaction parameter. This apparent interaction parameter can thus be calculated from experimental data of the equilibrium water uptake of the network in the presence of a vapour phase containing water, i.e., from the experimental sorption isotherm of the hydrogel.

For high water uptakes of the hydrogel a significant elastic expansion of the polymer network takes place, and the contribution to the chemical potential of this elastic force has to be taken into account in the free-energy equation of the system. When the sample is immersed in a liquid water environment the equilibrium uptake is determined by the thermodynamic equilibrium condition

$$\hat{\mu}_{\mathrm{w}}^{\mathrm{hydrogel}} = \mu_{\mathrm{w}}^{\mathrm{l}} \ , \tag{4}$$

where $\mu_{\mathrm{w}}^{\mathrm{l}}$ is the chemical potential of pure water in the liquid state. Equation (4) and the affine network model of rubber elasticity yield [4] the Flory–Rehner equation, which has been frequently applied to relate the average molecular weight of the effective strands between cross-links in the network, $\bar{M}_{\mathrm{e}}$, and the equilibrium water uptake from immersion in liquid water

$$\bar{M}_{\mathrm{e}} = -\frac{\rho V_{\mathrm{w}}\left[(1-\phi_{\mathrm{w}})^{1/3} - (1-\phi_{\mathrm{w}})/2\right]}{\ln\phi_{\mathrm{w}} + (1-\phi_{\mathrm{w}}) + \bar{\chi}(1-\phi_{\mathrm{w}})^2} \ , \tag{5}$$

where V_{w} is the molar volume of water and ρ is the density of the polymer. Equation (5) is calculated for a polymer network polymerised without solvent.

In the present article we address the interaction of water molecules and polymer chains in the case of poly(hydroxyethyl acrylate) (PHEA) hydrogels as a function of the cross-linking density of the network and as a function of the water content in the hydrogel. Water in hydrogels has been inferred to exist in different states, usually referred to as "bound" and "free" according to the strength of the linking with the polymer molecules [5, 6]. However, this view has also been questioned in its most simplified traits [7, 8]. Here, we focus on the determination of the water–polymer interaction parameter and the information which can be extracted from its value. Data for the diffusion coefficient of water in these hydrogels are reported as well. Previous studies have characterised the thermal, dielectric and water sorption properties of this polymer [8–12].

Experimental

The PHEA networks were block polymerised between glass plates to form sheets approximately 1-mm thick. The monomer (hydroxyethyl acrylate from Aldrich, 96% pure) was used without further purification. Ethylene glycol dimethacrylate (EGDMA, Aldrich 98% pure) was used as a cross-linking agent and 0.13 wt% benzoin (Scharlau 98% pure) was added as a photoinitiator. Polymerisation took place at room temperature for 24 h under UV irradiation. The low-molecular-weight substances remaining in the sample after polymerisation were extracted boiling in ethanol for 24 h and then the samples were dried at 80 °C in vacuo to constant weight. A series of samples was prepared starting from a mixture of HEA and EGDMA monomers in 99/1, 95/5 and 90/10 weight ratios, which will be called hereafter samples S1, S5 and S10, respectively.

Equilibrium water sorption isotherms were measured at 25 and 40 °C. The samples were allowed to equilibrate to constant weight (until the sample weight change was less than 10^{-4} g) in various desiccators where the RH was kept constant between 0.06 and 0.97 using different saturated salt solutions [13]. The water content, h, defined as the ratio of the weight of water to the weight of the dry sample, was determined by weighing.

Dynamic water sorption experiments were carried out by allowing the dry sample to equilibrate until ambient RH at 25 °C on the pan of an analytic balance (Sartorius A200 S) while its weight was being recorded continuously. Dynamic desorption experiments were conducted in the same way with a sample previously equilibrated in environments with RHs of 1, 0.94 or 0.69 at room temperature. Other dynamic sorption experiments were conducted by immersing the dry sample in distilled water at 10, 25 and 55 °C and measuring its weight, at selected immersion times, after gently drying the sample's surface with filter paper.

Dynamic–mechanical spectroscopy was performed using a Seiko DMS 210 apparatus at a frequency of 1 Hz and a heating rate of 2 K/min. The temperature dependence of the storage modulus, E', the loss modulus, E'', and the loss tangent, tan δ, was measured from −140 to 150 °C.

Results and discussion

Dynamic–mechanical analysis

The dynamic–mechanical relaxation spectrum of the three PHEA networks is shown in Fig. 1. The maximum of the loss tangent associated with the main relaxation appears at 38 °C in the network cross-linked with 1% EGDMA and shifts to higher temperatures with increasing cross-link density of the network (44 and 53 °C for 5 and 10% EGDMA, respectively). This is expected since the cooperative conformational rearrangements of the main chains become more difficult as the cross-linking density increases. The value of the elastic modulus at temperatures higher than the main relaxation, in the plateau region corresponding to the rubberlike behaviour, E'_{e} is a slightly increasing function of the temperature. According to the theory of rubber elasticity this value permits the calculation of the mean molecular weight between cross-links of the elastically active chains, $\bar{M}_{\mathrm{e}}$, as

$$\bar{M}_{\mathrm{e}} = \frac{\rho RT}{G_{\mathrm{e}}} \tag{6}$$

where G_{e} is the shear modulus in the elastomeric region, which can be estimated as $G_{\mathrm{e}} = E'_{\mathrm{e}}/3$, ρ is the density and R is the gas constant. Equation (6) is calculated using the affine network model, as in Eq. (5). The increase in E'_{e} with increasing temperature is due to the increase in the

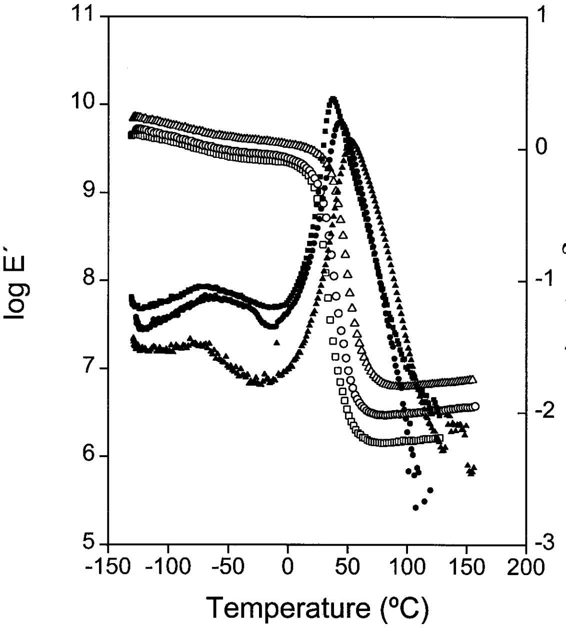

Fig. 1 Temperature dependence of the real part of the elastic modulus (*open symbols*) and the loss tangent (*filled symbols*) of poly(hydroxyethyl acrylate) (*PHEA*) samples S1 (■), S5 (●) and S10 (▲)

product ρT. Equation (6) was applied using the value of the density measured at 25 °C, which was the same for the three networks (1.312 g/cm^3), and the value of the elastic modulus at the same temperature obtained by linear extrapolation to 25 °C of the experimental data of the rubberlike region. The values of $\bar{M}_e$ thus calculated are given in Table 1. The mean number of monomeric units between cross-links of the elastically active strands, $\bar{n}_e$, decreases as the amount of EGDMA in the initial mixture of monomers increases. For a perfect network the number of monomers between cross-linking points expected from stoichiometry, $\bar{n}_{st}$, is half the ratio of the HEA and EGDMA mole numbers, since the cross-linker is tetrafunctional. Table 1 shows that $\bar{n}_e < \bar{n}_{st}$ for sample S1, which means that entanglements contribute to the elastic response. For samples S5 and S10, however, the situation is $\bar{n}_e > \bar{n}_{st}$, which means that the number of cross-linker molecules lost in inelastic joints increases rapidly with cross-linker concentration in the reacting mixture [4]. The peak in the loss tangent corresponding to the main relaxation broadens as the cross-linking density increases, which can be interpreted in the sense that there is a broader distribution of the mobilities or the relaxation times of the chain segments that contribute to conformational rearrangements. This could imply a broader distribution of the lengths of the elastic chains between cross-links as well.

At temperatures below the main relaxation, in the glassy state, a secondary relaxation, usually called γ relaxation both in PHEA [9–11, 14] and poly(hydroxyethyl methacrylate) [15–17], appears around −75 °C. This relaxation process is ascribed to local motions within the side-chain group. The presence of very small amounts of water absorbed produces a new relaxation peak, β_{sw} [9–11, 14–17], at temperatures higher than those of the γ relaxation, caused by the association of two side-chain groups to a water molecule through hydrogen bonding, thus producing a bulkier molecular group of more reduced mobility, which relaxes at a higher temperature [15–17]. The small shoulder in the high temperature side of the γ relaxation of sample S5 can be thus ascribed to the presence of traces of water in this sample after the drying process. Since this relaxation has already been thoroughly discussed [9–11], no further characterisation of it is pursued here.

Table 1 Characteristic parameters of the poly(hydroxyethyl acrylate) (*PHEA*) network as a function of the content of ethylene glycol dimethacrylate (*EGDMA*). $\bar{M}_e$: average molecular weight between cross-links of elastically active chains; $\bar{n}_e$: average number of HEA monomer units between cross-links in elastically active chains; n_{PHEA}/n_{EGDMA}: molar ratio of HEA to EGDMA monomers in the polymerisation mixture; $\bar{n}_{st}$: average number of HEA monomers between cross-links according to stoichiometry in a perfect network; h_m, c, f: parameters of the Guggengeim–Anderson–de Boer (*GAB*) equation (see text); n_m: number of primary sorption sites per HEA monomer unit in the network; α_l: number of water molecules per HEA unit corresponding to the water content h_l, calculated according to Eq. (10)

EGDMA content	1%	5%	10%
n_{PHEA}/n_{EGDMA}	168.9	32.4	15.4
$\bar{M}_e$	7930	3880	1880
$\bar{n}_e$	68.4	33.4	16.2
$\bar{n}_{st}$	84.5	16.2	7.7
Parameters of GAB equation at 25 °C			
h_m	0.055	0.050	0.047
c	1.82	2.17	2.21
f	0.87	0.86	0.86
n_m	0.36	0.34	0.34
Parameters of GAB equation at 45 °C			
h_m	0.041	0.037	0.035
c	2.74	2.96	2.84
f	0.96	0.95	0.95
n_m	0.27	0.25	0.25
Equilibrium water uptake in immersion			
h_l	2.00	1.16	0.68
α_l	14.3	13.6	13.0

Equilibrium sorption isotherms

The sorption isotherms show a small but significant decrease in the equilibrium water uptake of the network with increasing cross-linking density, as shown in Fig. 2. This is not an unexpected fact since the number of hydroxyl groups per unit mass of the sample decreases as the amount of hydrophobic cross-linking agent

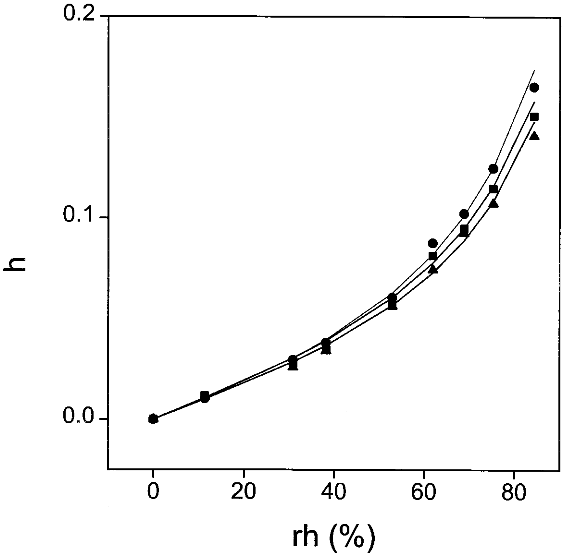

Fig. 2 Equilibrium sorption isotherms of PHEA samples at 25 °C. S1 (●), S5 (■) and S10 (▲) in terms of the water content of the sample against water activity. The *solid lines* correspond to the prediction of the Guggengeim–Anderson–de Boer equation

monomer increases. A quantitative analysis of this feature can be tried with the Guggengeim–Anderson–de Boer (GAB) multilayer sorption theory (see Ref. [18] and the references cited therein), which renders a relationship between the equilibrium water content of the hydrogel, h, (measured, for example, as the weight of water divided by the weight of the dry polymer) and the activity of water, a_w, inside it, in the form of an equation with three adjustable parameters:

$$\frac{h}{h_m} = \frac{cfa_w}{(1 - fa_w)[1 + (c - 1)fa_w]}. \tag{7}$$

Here h_m is the weight of the water molecules attached to sorption sites directly on the polymer chains (first sorption layer) referred to the unit weight of dry polymer, c is a parameter related to the energy difference between the water molecules of the first sorption layer and those absorbed in successive layers and f measures the energy difference between water molecules absorbed in the second and successive layers and the free water molecules of the surrounding environment. The parameters of Eq. (7) for the three PHEA networks studied in this work were determined by the two-step method recommended in Ref. [18] and are given at two temperatures in Table 1. The full lines in Fig. 2 show the prediction of the GAB equation with these parameter values. At constant temperature the decrease in h with increasing cross-linking density is correlated to the decrease in the number of water molecules absorbed in the first absorption layer, h_m. Since the cross-linking EGDMA monomers have hydrophobous character, it is safe to assume that the primary sorption sites are in the hydrophilic HEA monomeric units, and thus the increase in the degree of cross-linking is reflected in a slight decrease in h_m. The effect of increasing temperature is also to lower h_m, which means that the sorption process is an exothermic one. This is also consistent with the trend displayed by the parameter f of the GAB equation: values of f less than unity mean that the adsorbed water molecules have a lower free energy than the water molecules of the surrounding environment, and thus their adsorbed state is more stable. Table 1 shows that at a constant temperature f is not significantly dependent on the degree of cross-linking, whereas the increase in temperature makes the adsorbed layers less stable and f becomes closer to unity. As regards parameter c, its values are normal for hydrogels and polyelectrolytes [18], but their physical significance is less direct and usually more difficult to explain [18–20]; in our case it shows an increasing trend, slight with cross-linking density and more pronounced with temperature, as it should, since this means a loosening of the interaction between the sorbed water molecules and the substrate [18], but we cannot attempt a more thorough explanation of it.

From the value of the parameter h_m it was also possible to calculate the number of primary sorption sites in each HEA segment:

$$n_m = \frac{M_{HEA}h_m}{M_w w_{PHEA}}, \tag{8}$$

where M_{HEA} and M_w are the molecular weights of the repeating HEA unit and water, respectively, and w_{PHEA} is the weight fraction of HEA monomeric units in the network, which is assumed to be equal to the initial weight ratio of monomers in the polymerisation process. The value of n_m in sample S1 is 0.358 molecules of water absorbed in the first layer per monomeric PHEA unit at 25 °C and 0.267 at 45 °C. In samples S5 and S10 the values of n_m are nearly equal and slightly but significantly smaller than in sample S1. These numbers mean that not every hydroxyl group of the HEA monomer is available as a primary sorption site for a water molecule, probably because a number of them are mutually linked in inter- or intramolecular hydrogen bonds and are thus not accessible to water molecules, and that this effect increases slightly with cross-linking density.

In the water activity regime $a_w < 1$, where the network expansion effects are still negligible and water molecules and chain segments are randomly mixed together, Eq. (3) was employed to calculate the Flory–Huggins water–polymer apparent interaction parameter $\bar{\chi}$. The volume fraction of water in the hydrogel was calculated from the known weight fraction, h, as

$$\phi_w = \frac{h}{h + v_{net}/v_w}. \tag{9}$$

Here v_{net} and v_{w} are the specific volumes of the dry network and of water, respectively, and no excess volume is assumed for the polymer–water blend. Discrepancies between the experimental behaviour and the Flory–Huggins equation are expected to occur at small water contents owing to the hydrogen bonding between water molecules and polymer polar groups, since the Flory–Huggins theory rests on a purely combinatorial expression for the entropy of mixing which disregards any effect of the interaction between the components of the mixture on their available states. In this interval of low water contents an increase in the interaction parameter with water content has been reported [12, 19, 20]; for higher water contents decreasing values of $\bar{\chi}$ with water content have been found [12, 20]. The values of the apparent interaction parameter calculated with Eq. (3) for water activities between 0.4 and 0.94 are shown in Fig. 3. $\bar{\chi}$ decreases when the volume fraction of water in the hydrogel increases. In spite of the scattering of the data shown in Fig. 3, a slight increase in the apparent interaction parameter with increasing cross-linking density can be deduced, which is explained by the decreasing hydrophilicity of the network with increasing content of the hydrophobic cross-linking agent. The same feature was found in Refs. [21, 22] in hydrogels cross-linked with hydrophobic cross-linkers.

The water uptake from the vapour phase with RH < 1 is limited because no bulk water domains can be formed in the sample, since the phase constituted by these pure water domains would not be in thermodynamical equilibrium with the water of the vapour phase environment. Thus, the water content for water activities less than unity is lower than approximately 0.3. In PHEA samples containing higher amounts of water the presence of bulk water has been detected in differential scanning calorimetry experiments by its freezing and melting peaks [8, 9]. These higher water contents in the hydrogels correspond in our case to the immersion of the samples in a liquid water environment and give rise to the full points in Fig. 3, which are commented on after the presentation of the immersion results.

Sorption from liquid water

The amount of water absorbed by the samples immersed in water as a function of time is shown in Fig. 4. It can be observed that the sorption process is the result of the overlapping of two different kinetics. A first sorption stage yields a plateau region, for times ranging between 10 and 100 h, and after that period the sample weight starts increasing again. Clearly the amount of water absorbed decreases as the average molecular weight between cross-links decreases. It can be supposed that the first sorption stage could correspond to the initial value of $\bar{M}_{\mathrm{e}}$, while the second stage would be explained by a process associated with a continuous decrease in $\bar{M}_{\mathrm{e}}$ with time, which could be due to the breaking of intramolecular hydrogen bonds with the expansion of the network, allowing further expansion of the network, or even to the breaking of main chain bonds during the expansion process. Any of these phenomena would have kinetics much different from the water diffusion itself and would allow a continuous increase in water uptake with time. Additional experimental work is necessary to settle this question. Figure 4 shows that the equilibrium values (h_{l} in Table 1) of the

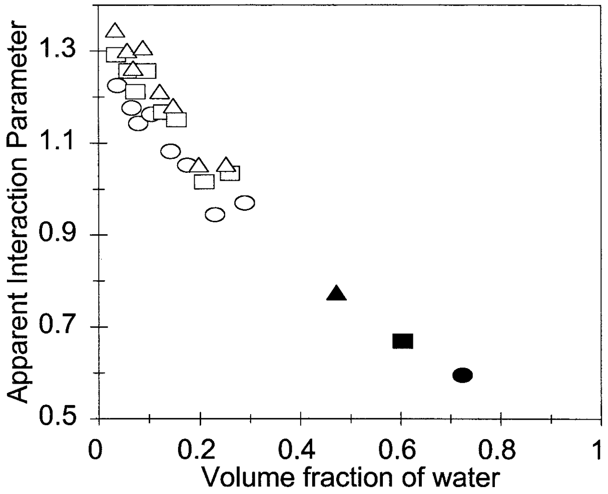

Fig. 3 Water content dependence of the apparent interaction parameter in samples S1 (●), S5 (■) and S10 (▲). The *open symbols* represent the values calculated from the equilibrium sorption isotherms using Eq. (3), while the *filled symbols* are the values calculated from the immersion experiments using Eq. (5)

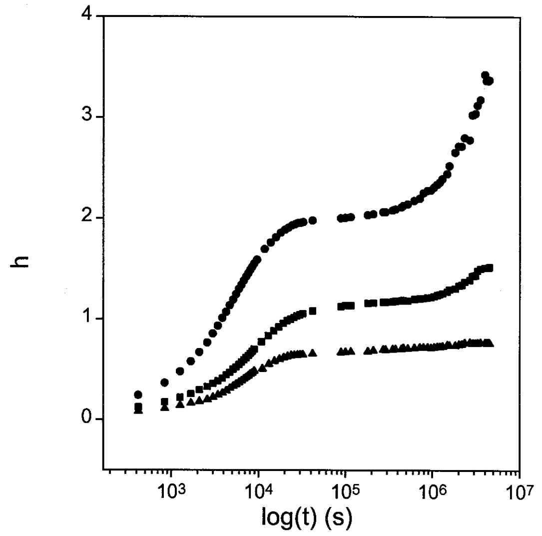

Fig. 4 Water uptake as function of time in samples S1 (●), S5 (■) and S10 (△) immersed in liquid water at 25 °C

water uptake in immersion greatly exceed those reached during sorption from a vapour phase. The difference is that now a bulk water phase residing in the hydrogel micropores can exist from a thermodynamical point of view. As said previously, the results of the immersion experiments yield the values of the apparent Flory–Huggins interaction parameter corresponding to high volume fractions of water in the hydrogel. Since for these water uptakes the expansion of the network becomes significant, $\bar{\chi}$ must now be calculated with Eq. (5). In it, the values of $\bar{M}_e$ were taken from the dynamic–mechanical results, Eq. (6), and the volume fraction of water in the sample was calculated from the water uptake after immersion for 10^5 s (h_l data given in Table 1). The values of the apparent interaction parameter thus calculated are shown as the full symbols in Fig. 3. It can be observed that now the three points corresponding to the three different networks seem to fall on the same line, which would be a common prolongation of the three tendency lines obtained at the lower water contents (open symbols in Fig. 3). The amount of water absorbed in the form of bulk water domains is now much higher than that forming a homogeneous phase with PHEA ($h < 0.3$). The former depends more on the elasticity of the network, while the latter depends more on the number of sorption sites in the polymer chains. The relative importance of these two factors for the differently cross-linked networks can be clearly appreciated when one compares their maximum h values attainable in sorption from a vapour phase (extrapolation to $a_w = 1$ in Fig. 2) with those attainable in immersion (h_l values in Table 1): whereas the latter almost double from sample to sample and span the range from 0.68 to 2.00 the former would all lie in the vicinity of 0.3. Thus, the amount of cross-linking agent in the network has little influence on $\bar{\chi}$ for high volume fractions of water, and the values obtained for the three samples are representative of the same water content dependence of the apparent interaction parameter between water molecules and polymer chains. This consistency of both determination methods for $\bar{\chi}$ is a remarkable result of the present study. The decreasing trend which on the whole Fig. 3 shows for the apparent interaction parameter can also be explained on the basis of the picture of the hydrogel here advanced. The Flory–Huggins interaction parameter should, in principle, be independent of composition, but it was already observed by Flory [3] that this condition, required by the theory, was only exceptionally met in experimental behaviour. The interaction parameter is a normalised interaction enthalpy which supposes that the nature of the pair interactions is not altered when the concentration of one of the components of the system changes. However in a hydrogel one must concede that the interaction of a given water molecule with another water molecule or with one of the polymer units might be different depending on the intensity of that molecule's link to a polymer chain (i.e., whether it is adsorbed in the first or in successive layers, or not adsorbed at all) or on the degree to which the polymer unit is screened by surrounding water molecules, and this depends on concentration. This introduces a dependence of $\bar{\chi}$ on the water volume fraction. Moreover, the number of water molecules per HEA monomer, α, which corresponds to a water content h in the hydrogel is

$$\alpha = h\frac{M_{\mathrm{HEA}} + (n_{\mathrm{EGDMA}}/n_{\mathrm{HEA}})M_{\mathrm{EGDMA}}}{M_{\mathrm{w}}}, \tag{10}$$

with M_{w}, M_{HEA} and M_{EGDMA} the molecular weights of water, HEA and EGDMA, respectively, and $n_{\mathrm{EGDMA}}/n_{\mathrm{HEA}}$ the molar ratio of EGDMA and HEA monomers in the polymer network (Table 1). The ratio α starts being 0 at zero water volume fraction, has a value around 2 at the maximum water uptakes from the vapor phase and attains values around 14 for the water contents corresponding to immersion (Table 1). Thus, as the water volume fraction in the hydrogel increases, the kind of pair interactions which statistically predominate starts to be the water–water interaction, which explains why $\bar{\chi}$ decreases (this means, in general, an increase in solubility [3] and, in the case of a hydrogel, in hydrophilicity), tending towards the value which would correspond to an ideal mixture (perfect solubility), $\bar{\chi} = 0.5$ (at high water volume fractions χ no longer depends on concentration, and $\bar{\chi}$ coincides with χ). As discussed later, this same fact is reflected in the behaviour of the water diffusion coefficient.

Water diffusion

The solution of Fick's second law,

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{11}$$

where c is the concentration of water in the polymer sample, x is distance, t is time and D the diffusion coefficient, can be approximated for short times in the case of the diffusion through a sheet with thickness l by the equation

$$\frac{\Delta m_t}{\Delta m_\infty} = \frac{4}{\sqrt{\pi}}\sqrt{\frac{tD}{l^2}}, \tag{12}$$

where Δm_t and Δm_∞ are the weight gains (in the case of a sorption experiment) or losses (in desorption) of the sample at time t and at equilibrium, respectively [23]. As a consequence, the reduced weight change $\Delta m_t/\Delta m_\infty$ must be a linear function of the square root of time in the initial stage of the sorption or desorption process. The slope of $\Delta m_t/\Delta m_\infty$ versus $\sqrt{t}$ allows the calculation of D.

Three desorption experiments were carried out at 28 °C at ambient RH, starting from samples which initially contained an amount of water corresponding to water activities of 1, 0.94 and 0.69, respectively. The reduced desorption curves for sample S1 are shown in Fig. 5. The dependence of the slope of this diagram with the initial water content of the sample is an indication that there is a significant dependence of the diffusion coefficient, *D*, on water concentration. The explanation here runs parallel to that given for the interaction parameter: the environment "seen" by a diffusing water molecule is different depending on the degree of hydration of the medium. This feature indicates that the diffusion process is not Fickian. Curves nearly identical to those shown in Fig. 5 were obtained in samples S5 and S10. Anyway, values for the parameter *D*, considered now as an apparent diffusion coefficient, were calculated from the linear part of the plot in the region where $\Delta m_t/\Delta m_\infty < 0.5$ and are shown in Table 2. The same values are valid for samples S5 and S10. The values of *D* calculated from the initial stages of a sorption experiment, where water molecules can be thought to diffuse through a still essentially dry medium, are smaller than those determined in the desorption experiments, and in the latter *D* increases with the initial water content of the sample. This means that the diffusion of water molecules is hindered by their interaction with the hydrophilic groups of the polymer chains. As these sorption sites become progressively occupied by water molecules during the hydration process that interaction is screened by the very water molecules of the successive sorption layers. The diffusion of a water molecule then becomes easier, a fact reflected in the decrease in the diffusion coefficient.

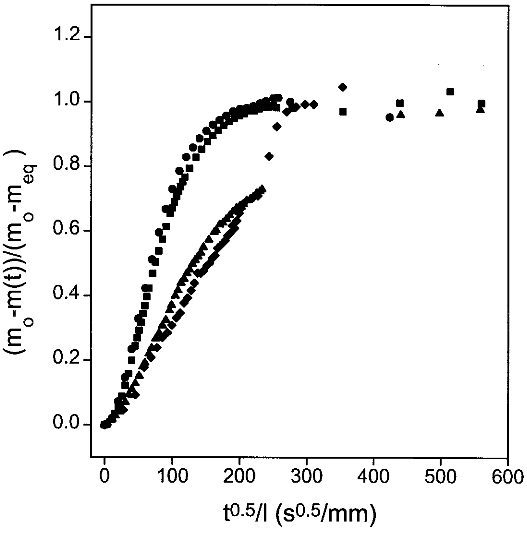

Fig. 5 Plot of the reduced weight change against the reduced time [see Eq. 12] of sample S1 in a sorption experiment (◆) and in desorption experiments starting with the sample equilibrated in a vapour atmosphere with a relativity humidity of 1 (●), 0.94 (■) and 0.69 (▲)

Table 2 Apparent diffusion coefficient calculated for sample S1 in sorption experiments and desorption experiments starting with the sample equilibrated in a vapour atmosphere with different relative humidities (*RH*)

	D (10^7 cm^2 s^{-1})
Sorption	0.22
Desorption RH = 0.69	0.69
Desorption RH = 0.94	1.4
Desorption RH = 1	1.6

Conclusions

The interaction of water molecules and a hydrophilic polymer network of PHEA has been studied as a function of the degree of cross-linking of the network and of the concentration of water absorbed. The combined use of sorption isotherms, immersion experiments and dynamic–mechanical spectroscopy has allowed the determination of the Flory–Huggins interaction parameter, as well as other parameters which characterise the state and intensity of bonding of the water molecules in the hydrogel. Water sorption is an exothermal process in these systems. The state of the sorbed water molecules depends on their activity: for activities less than 1 water molecules cannot (for thermodynamical reasons) form domains of bulklike liquid behaviour inside the hydrogel; they reside in the network randomly mixed with the polymer units. Under these conditions the amount of absorbed water is limited to a maximum of some two molecules per monomer unit and depends only slightly on the cross-linker content. The network has a limited expansion, reflected by the fact that the primary sorption sites available to water molecules are of the order of one for each three monomer units, almost independent of the cross-linker content. When the network is equilibrated in a liquid water environment (activity of 1) bulk water domains can exist and they expand the network to be accommodated in nanopores. The network can then contain a number of the order of 14 water molecules per monomer unit. The values of the interaction parameter must be calculated independently in both sorption regimes, owing to the fact that the free energy of the system has different contributions in both situations. They display a strong dependence on the concentration of water in the network: they start being high at low hydrations and fall to figures characteristic of high hydrophilicity when the water volume fraction in the hydrogel approaches unity.

Acknowledgement J.L.G.R. and M.M.P. acknowledge the support of the CICYT through projects MAT97-0634-C02-01 and MAT99-0509.

References

1. Peppas NA, Moyhiman HJ (1987) In: Peppas NA (ed) Hydrogels in medicine and pharmacy, vol 2. Wiley, New York, p 49
2. Ozawa H, Hosaka S, Kuminoto T, Tanzawa H (1988) Biomaterials 5:170
3. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, Ithaca
4. Erman B, Mark JE (1997) Structure and properties of rubberlike networks. Oxford University Press, Oxford
5. Barnes A, Corkhill PH, Tighe BJ (1988) Polymer 29:2191
6. Smyth G, Quinn FX, McBrierty VJ (1988) Macromolecules 21:3198
7. Roorda W (1994) J Biomater Sci Polym Ed 5:383
8. Rault J, Lucas A, Neffati R, Monleón Pradas M (1997) Macromolecules 30:7866
9. Kyritsis A, Pissis P, Gómez Ribelles JL, Monleón Pradas M (1994) J Non-Cryst Solids 172–174:1041
10. Kyritsis A, Pissis P, Gómez Ribelles JL, Monleón Pradas M (1994) J Polym Sci Polym Phys Ed 32:1001
11. Kyritsis A, Pissis P, Gómez Ribelles JL, Monleón Pradas M (1995) Polym Gels Networks 3:445
12. Gómez Ribelles JL, Monleón Pradas M, Gallego Ferrer G, Peidro Torres N, Pérez Giménez V, Pissis P, Kyritsis A (1999) J Polym Sci Polym Phys Ed 37:1587
13. Greenspan L (1977) J Res Natl Bur Stand (US) 81A:89
14. Janáček J, Kolařík J (1965) Collect Czech Chem Commun 30:1597
15. Janáček J, Kolařík J (1967) J Polym Sci C 16:279
16. Lednický F, Janáček J (1971) J Macromol Sci B 5:335
17. Gómez Ribelles JL, Meseguer Dueñas JM, Monleón Pradas M (1988) Polymer 29:1125
18. Timmermann EO (1989) J Chem Soc Faraday Trans 1 85:1631
19. Galin JC, Galin M (1992) J Polym Sci Polym Phys Ed 30:1113
20. Galin JC, Galin M (1995) J Polym Sci Polym Phys Ed 33:2033
21. Davis TP, Huglin MB, Yip DCF (1988) Polymer 29:701
22. Good WR, Cantow H (1979) J Macromol Chem 180:2605
23. Crank J, Park GS (eds) (1968) Diffusion in polymers. Academic, London