Colloid Polym Sci (2005) 283: 681–690
DOI 10.1007/s00396-004-1208-y

ORIGINAL CONTRIBUTION

G. Gallego Ferrer
J. M. Soria Meliá
J. Hernández Canales
J. M. Meseguer Dueñas
F. Romero Colomer
M. Monleón Pradas
J. L. Gómez Ribelles
P. Pissis
G. Polizos

Poly(2-hydroxyethyl acrylate) hydrogel confined in a hydrophobous porous matrix

Received: 6 May 2004
Accepted: 16 August 2004
Published online: 22 October 2004

G. Gallego Ferrer · J. M. Soria Meliá
J. Hernández Canales
J. M. Meseguer Dueñas
F. Romero Colomer
M. Monleón Pradas
J. L. Gómez Ribelles (✉)
Centre for Biomaterials,
Universidad Politécnica de Valencia,
Camino de Vera s/n, 46071 Valencia, Spain
E-mail: jlgomez@ter.upv.es
Tel.: +34-96-3877275
Fax: +34-96-3877276

P. Pissis · G. Polizos
Department of Physics,
National Technical University of Athens,
Zografou Campus, 15780 Athens, Greece

Abstract A series of interpenetrated polymer networks (IPNs) in which the first component is a porous poly(ethyl methacrylate) (PEMA) hydrophobic network and the second one is a poly(2-hydroxyethyl acrylate) (PHEA) hydrophilic network were synthesized. Equilibrium sorption isotherms can be reduced to a single master curve for all the IPNs when the water absorbed is expressed per gram of PHEA in them. The equilibrium water sorption in immersion is always much smaller than that of pure PHEA. This feature is due to the confining effect of the stiff PEMA matrix. The plasticizing effect of the absorbed water on the PHEA phase was characterized using thermally stimulated depolarization currents, dynamic-mechanical analysis and dielectric relaxation spectroscopy. The results show that the shift of the main relaxation peak towards lower temperatures is unaffected by the presence of the PEMA matrix, and only depends on the water content per gram of PHEA in the IPN.

Keywords Interpenetrated polymer networks · Hydrogels · Water sorption isotherms · Dynamic-mechanical analysis · Plasticization

Introduction

Polymer hydrogels are macromolecular networks which imbibe large amounts of water without dissolving, and because of this they have found a large number of applications, ranging from agriculture to medicine and pharmacy [1–3]. Their good biocompatibility and water permeation properties are the basis of these applications. The main handicap of hydrogels is their poor mechanical properties, mainly in the swollen state. Consequently, reinforcement is needed for their applications. Increasing the cross-linking density, copolymerization with a more resistant hydrophobic network and crystallization (when possible) are among the ways to reinforce hydrogels as well as the formation of interpenetrating polymer networks [4], interpenetrated polymer networks (IPNs), with two polymers: a hydrophilic one and a hydrophobic one, which is the option chosen in the present work. It is known that combination of a hydrophilic and a hydrophobic polymer forming microphase-separated structures is a way for reinforcing hydrogels [5]; this method takes advantage of the behaviour of hydrophobic polymer in the presence of water. The hydrophobic domains act as additional linking points in the hydrogel network, improving mechanical properties. Besides, it has been shown [6] that the alternating microdomain structure shows excellent antithrombogenic properties, and blood compatibility of the resulting materials is enhanced.

The structural heterogeneity of the IPNs commented above is due to the development of thermodynamical instability of the homogeneous mixture during polymerization process, as a consequence of the growing molecular weight of at least one of the components in the case of sequential IPNs, those synthesized in the present work. The phase morphology of an IPN depends on several factors: miscibility of the components, composition, cross-linking density and the kinetic details of the reaction. Although all these factors are important when a sequential IPN is prepared, it has been verified that the cross-linking density of the first network is the determinant factor in the morphology that is finally obtained [7, 8]. When one of the networks is a hydrophilic polymer, the resulting IPN can form hydrogels when swollen in water, and the properties sought for in applications, which rest upon water uptake and transport inside the hydrogel, may be affected by the phase micromorphology of the IPN. In this paper we study a sequential IPN formed by a first hydrophobous porous poly(ethyl methacrylate) (PEMA) network and a second hydrophilic poly(2-hydroxyethyl acrylate) (PHEA) network polymerized in the presence of different quantities of solvents (PEMA(sponge)-*i*-PHEA IPNs). We consider the effect of changing IPN composition upon water diffusion and sorption, and on the phase organization and the morphology of the first porous network, which can be inferred from these data and from thermally stimulated depolarization currents (TSDC), dynamic-mechanical analysis and dielectric relaxation spectroscopy (DRS) at different water contents in the samples.

Previous work on hydrogel-forming networks refers mostly to poly(hydroxyethyl methacrylate) [9], polyacrylamide, poly(acrylic acid) [10] and poly(vinyl alcohol). PHEA is more hydrophilic than poly(hydroxyetyl methacrylate). The innovation of this study in relation to the previous work is that the hydrophilic component, the PHEA network, is confined in a rigid (at room temperature) sponge prepared with different quantities of diluent, and it has been possible to relate the morphology of the confining sponge with the sorption properties of the resulting IPNs.

Materials and methods

Different sequential IPNs of porous PEMA, PEMA(sponge), and PHEA were polymerized with the same quantity of cross-linker in both networks (1% of ethylene glycol dimethacrylate, EGDMA, relative to monomer weight). The first network was polymerized in a porous form using different quantities of ethanol as porogen. Two types of solutions of EMA monomer (Aldrich 99% pure) with a 1% by weight of EGDMA as cross-linking agent, a 2% by weight of benzoin as photoinitiator and two different ethanol contents 40 and 60% by weight (relative to monomer/diluent mixture) were prepared and polymerized at room temperature under ultraviolet radiation for 24 h between two glass plates. The resulting PEMA porous networks were boiled in ethanol for 1 day to extract the remaining low molecular weight substances. The rinsed samples were introduced and swollen to equilibrium in three types of solutions: the first one contained HEA monomer (Aldrich 96% ethanol), a 1% by weight of EGDMA and a 0.2% of benzoin; the second and third ones consisted of a mixture of HEA monomer (with the same quantities of cross-linker and initiator as the first one) and a 60 or 80% by weight (relative to monomer/diluent mixture) of ethanol, respectively. Then, polymerization of the second network took place as explained for the first one. Low molecular weight substances were extracted in boiling ethanol for 1 day and the resulting IPNs were dried *in vacuum* to constant weight firstly at 120 °C and afterwards at 170 °C. The weight fraction of the PHEA network in the IPNs, x_{PHEA}, is shown in Table 1.

Water sorption isotherms for the IPNs were determined at 45 °C by the standard method [11, 12] of equilibrating the samples in ambients of controlled and known relative humidities (RH): the samples were allowed to equilibrate to constant weight in various thermostatized sealed dessicators over saturated water solutions of different salts in an oven. A Sartorius A200S balance with 10^{-4} g sensitivity was employed for these measurements.

Water diffusion in immersion in liquid water for the IPNs was analysed at 45 °C by placing the dry samples in liquid water and weighing them at selected times after carefully drying their surface with filter paper.

Thermally stimulated depolarization currents of the hydrated samples were measured using a Keithley 610 electrometer [13, 14]. Small discs of the samples of 15 mm in diameter and around 1 mm in thickness were inserted at room temperature between the plates of a capacitor and polarized by the application of a DC electric field between 300 and 600 V (depending on the thickness of the sample) at room temperature for 5 min. With the electric field still applied, the sample was quenched to −170 °C and short-circuited. The depolarization current was measured on heating at a rate

Table 1 Composition of the PEMA(sponge)-*i*-PHEA IPNs

IPN	Weight fraction of ethanol in the polymerization of the PEMA network	Weight fraction of ethanol in the polymerization of the PHEA network	Weight fraction of PHEA in the IPN, x_{PHEA}
40/80	0.4	0.8	0.15
40/60	0.4	0.6	0.45
40/–	0.4	0	0.71
60/80	0.6	0.8	0.34
60/60	0.6	0.6	0.64
60/–	0.6	0	0.81

ranging between 3 and 4 °C min^{-1} until room temperature.

Dynamic-mechanical spectroscopy (DMS) of the dry and swollen samples was performed in a Seiko DMS 210 apparatus at the frequency of 1 Hz in the tension mode. The temperature dependence of the storage modulus (E'), loss modulus (E'') and loss tangent (tan δ) was measured from −130 to 170 °C at a rate of 2 K min^{-1}. The samples were prismatic, approximately $10 \times 4.5 \times 0.9$ mm^3.

Dielectric relaxation spectroscopy was performed with a Schlumberger Frequency Response Analyser FRA SI1 260. The sample was placed between two golden electrodes in a dielectric cell, which was introduced inside a cryostatic Novocontrol system. The samples were measured between 0.1 and 10^6 Hz every 10° in the appropriate temperature range for each sample.

Results

Figure 1a shows the experimental sorption isotherms (water uptake of the polymer, expressed as mass of water gained per unit mass of dry polymer, $w = m_1/m_2$, where subindex 1 corresponds to water and subindex 2 to the polymer) as a function of the water activity in the gel, a, for the PEMA(sponge)-*i*-PHEA IPNs and for the PHEA homonetwork. As explained above the experimental sorption isotherms are determined by equilibrating the samples in ambients of controlled and known RH and measuring their water uptake gravimetrically. The relative humidity in air atmosphere at pressure p and temperature T is the ratio of the partial pressure of the water vapour in the atmosphere, $y_1 \cdot p$, and the pressure of pure water at T, $p_1^{\mathrm{v}}(T)$,

$$\mathrm{RH} = \frac{y_1 p}{p_1^{\mathrm{v}}}$$

(y_1 is the molar fraction of water in the atmosphere). The sorption experiments are conducted at atmospheric pressure, $p = 1$ atm. At this pressure the gas mixture forming the atmosphere can be regarded as ideal, and the partial pressure of whatever its components is its fugacity: $y_1 p = \hat{f}_1^{\mathrm{v}}(1\,\mathrm{atm}, T)$. On the other hand, at 1 atm and T the fugacity of pure liquid water coincides with its vapour pressure: $f_1^{\mathrm{L}} = p_1^{\mathrm{v}}(T)$, and thus the relative humidity turns out to be the activity of water in the atmosphere, with reference to liquid water

$$\mathrm{RH} = \frac{\hat{f}_1^{\mathrm{v}}}{f_1^{\mathrm{L}}} = \hat{a}_1^{\mathrm{v}}.$$

Equilibrium of the gel in the gaseous environment demands equality of the chemical potential of water in the gel and in the environment:

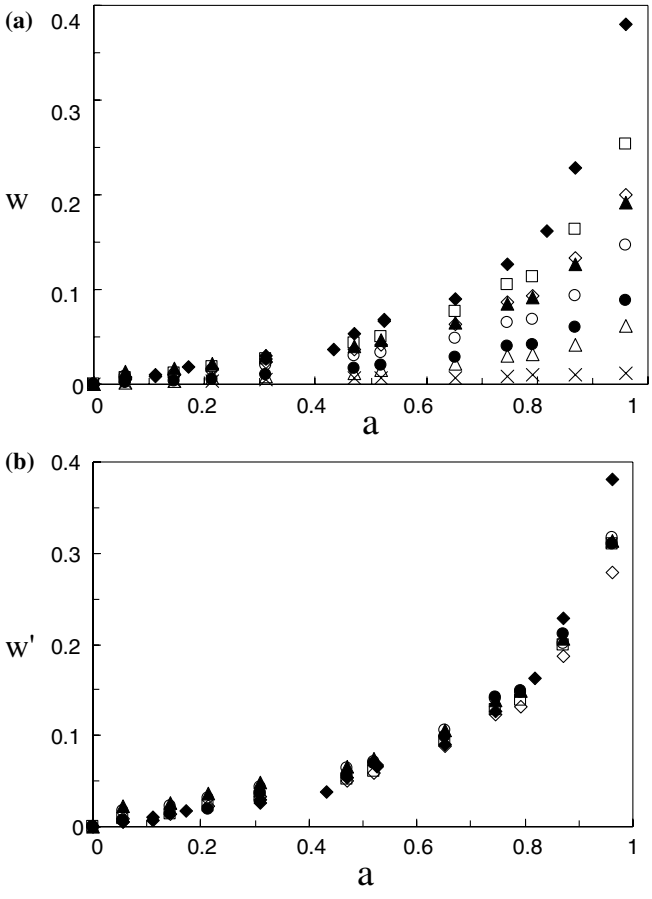

Fig. 1 Sorption isotherms at 45 °C for the PEMA(sponge)-*i*-PHEA IPNs (**a**). The Fig. **b** shows the isotherms displayed as mass fraction of sorbed water per unit PHEA mass in the IPN, w', against water activity, a. The samples are identified by their PHEA mass fraction equal to: 1 PHEA network (*filled diamond*), 0.81 (*open square*), 0.71 (*open diamond*), 0.64 (*filled triangle*), 0.45 (*open circle*), 0.34 (*filled circle*), 0.15 (*open triangle*) and 0 PEMA network (×)

$$\hat{\mu}_1^{\mathrm{gel}} = \hat{\mu}_1^{\mathrm{v}},$$

and this equality turns, by $\hat{\mu}_1 = \mu_1 + RT \ln \hat{a}_1$, into an equality between activities $\hat{a}_1^{\mathrm{gel}} = \hat{a}_1^{\mathrm{v}}$, such that,

$$\hat{a}_1^{\mathrm{gel}} = \mathrm{RH},$$

and the experimental isotherm determines, at each temperature, the relationship between composition and activity

$$w = w(a, T),$$

with $a = \hat{a}_1^{\mathrm{gel}}$, for the sake of clarity.

The sorption isotherms in Fig. 1a exhibit the convex shape characteristic of type III isotherms in the Brunauer classification [15]. For each constant water activity the water content in the IPNs increases with increasing mass fraction of the PHEA component in them.

In order to study the water transport properties in the hydrogels dynamic sorption, experiments in immersion in liquid water were performed and are shown in Fig. 2, where the water uptake of the polymer, w, is represented as a function of time, t, in a logarithmic scale. The plot shows that the equilibrium water content increases as the mass fraction of PHEA in the IPNs is increased.

Thermally stimulated depolarization current experiments were carried out on all IPNs with different water contents, and the results for all samples were similar. As an example Fig. 3 shows the spectra of the IPN with PHEA mass fraction, x_{PHEA}, equal to 0.81. The depolarization current has been normalized to

$$I_{\mathrm{n}} = \frac{I \cdot d}{V \cdot A \cdot b},$$

where I is the depolarization current in pA, d is the thickness of the sample in mm, V is the voltage in Volt, A the area of the sample in mm^2 and b the heating rate in K min^{-1}. This normalization makes it possible to compare thermograms obtained on samples of different thicknesses, with different voltages, areas and heating rates [14]. These spectra are very similar to those of pure PHEA [16]. For the lower water mass fractions three relaxations are observed, which have been called, in order of increasing temperature, the γ, β_{sw} and α relaxations following the references [17, 18]. As the magnitude of the single relaxation observed in the PEMA homopolymer in the temperature range of measurements in Fig. 3 (results not shown) is very small when compared with those of PHEA homonetwork [16] and those of the PEMA(sponge)-*i*-PHEA IPNs, these three relaxations have been attributed to the PHEA phase in the IPNs. The α relaxation, which occurs at higher temperatures, is ascribed to the main relaxation of the PHEA phase in the IPNs. This peak shifts to lower temperatures as the water content increases, and for the largest water contents it splits into two peaks, α and ρ. The origin of this new ρ peak is thought to be due to space charges, and its intensity depends on numerous factors such as the type of electrodes, impurities in the sample, etc. [14]. The γ relaxation, which shows up around 130 K, has been attributed to internal motions in the side chain of PHEA phase, which orient the dipole of the hydroxyl group [19]. The magnitude of this relaxation decreases with increasing water content, and from a certain humidity on it completely disappears. Its temperature shows no dependence on water content and remains constant. The β_{sw} relaxation happens at temperatures immediately higher than the γ, around 175 K for the scan with the lowest water content of the gel. With increasing amounts of water in the sample, this peak increases in magnitude and shifts to lower temperatures, until it completely overruns the γ peak.

The dynamic-mechanical experiments show in all the samples the presence of two α relaxations corresponding to the PEMA and PHEA phases. As a representative example, Fig. 4 shows the temperature dependence of the real part of the elastic modulus (Fig. 4a) and the loss tangent (Fig. 4b) of the IPN with PHEA mass fraction, x_{PHEA}, equal to 0.81 at different water contents. When the sample is nearly dry the peak of tan δ corresponding to the α relaxation of the PEMA phase appears at 102 °C while that corresponding to PHEA appears at 39 °C.

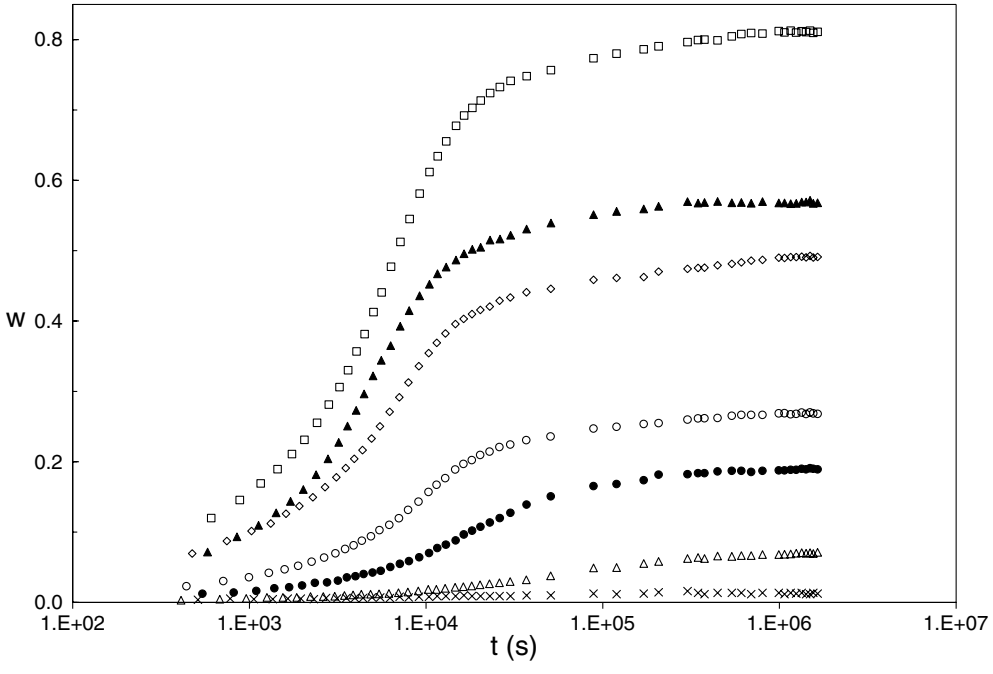

Fig. 2 Water uptake in immersion as a function of time (in a logarithm scale) at 45 °C for the PEMA(sponge)-*i*-PHEA IPNs, identified by their PHEA mass fraction equal to: 0.81 (*open square*), 0.71 (*open diamond*), 0.64 (*filled triangle*), 0.45 (*open circle*), 0.34 (*filled circle*), 0.15 (*open triangle*) and 0 PEMA network (×)

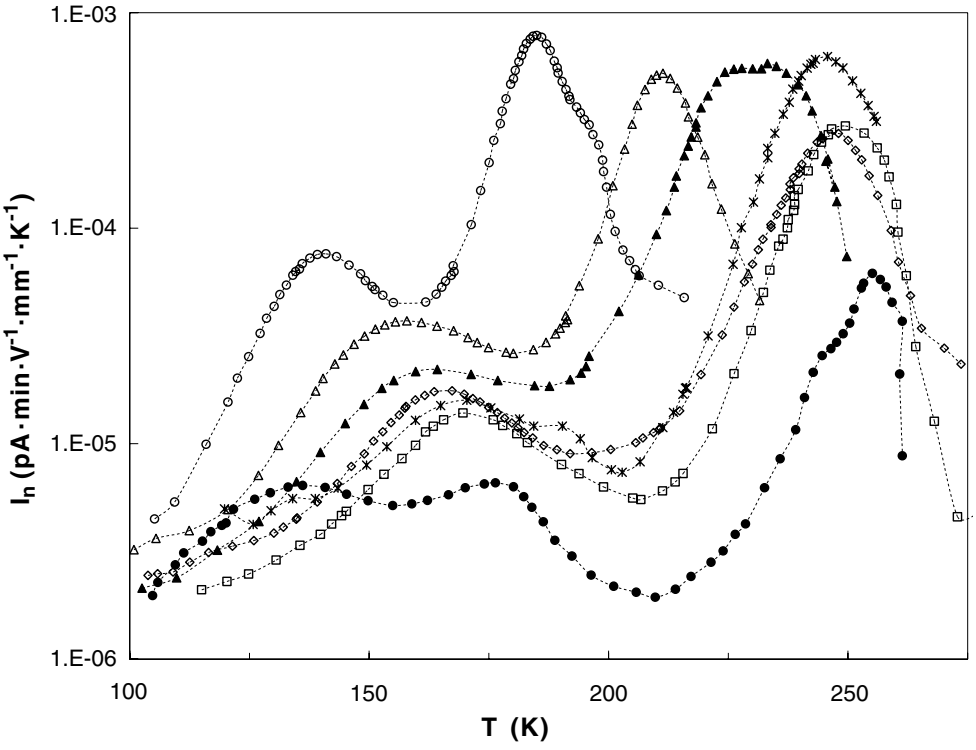

Fig. 3 TSDC thermogram of the IPN with PHEA mass fraction equal to 0.81 (PEMA sponge synthesized with 60% ethanol and immersed in PHEA monomer) with different water contents: $w = 0.0066$ (*filled circle*), $w = 0.0290$ (*open square*), $w = 0.0349$ (*), $w = 0.0366$ (*open diamond*), $w = 0.0814$ (*filled triangle*), $w = 0.1288$ (*open triangle*), $w = 0.2521$ (*open circle*)

At lower temperatures the secondary γ and β_{sw} relaxations take place.

The samples containing absorbed water were rapidly cooled down inside the equipment to −130 °C. No evaporation of water from the sample up to room temperature during the measuring scan is expected, but at higher temperatures water is rapidly lost by the sample and the results in the temperature interval of the main relaxation of PEMA are not representative of the wet samples.

As the amount of water increases the α relaxation corresponding to the PHEA phase shifts towards lower temperatures due to the plasticization of this phase. However, at the highest water contents, above 0.3 g of water per gram of PHEA in the sample, the temperature of the peak starts increasing. The loss tangent plots show a shoulder at the low-temperature side of the main peak of the PHEA phase that must be ascribed to the β_{sw} relaxation: the overlapping of the α relaxation and the scattering of the results in some cases prevents a detailed analysis of the secondary dynamic-mechanical relaxations, although they play an important role in the mechanical behaviour of the IPNs, as proved by the significant decrease of the elastic modulus with increasing temperature below −50 °C (Fig. 4a). A shoulder in the high-temperature side of the PHEA α relaxation can be due to the loss of water. Again, the E' plots are only significant up to room temperature in the wet samples. They show the plasticization of the PHEA phase up to a limit of water content, and then the main relaxation shifts towards higher temperatures and at the same time the values of the modulus in the glassy state are clearly higher than in samples with lower water contents. In the case of the sample whose spectra are shown in Fig. 4a, this behaviour corresponds to the sample containing 0.25 g of water per gram of sample, or 0.31 g of water per gram of PHEA.

Figure 5 shows the dielectric results obtained in an IPN with PHEA mass fraction equal to 0.15. The study of the influence of water on the α relaxations of the systems is difficult because of the overlapping of the ionic conductivity with the dipolar contributions corresponding to the conformational motions. In fact in all the samples containing more than 15 wt% of PHEA, the α relaxation of both phases was completely covered by the space charge contributions. In the case of the sample of Fig. 5 the plasticization of the PHEA phase is clearly observed, and the peak shown by the imaginary part of the dielectric permittivity shifts clearly towards lower temperatures as the water contents increases; but even in this case it is difficult to determine the temperature of the maximum because of the conductivity contribution at the high-temperature side of the peak. At low temperatures the β_{sw} shows the same behaviour described above for the TSDC results; these results correspond to the sample with PHEA mass fraction, x_{PHEA}, equal to 0.81, because the effect of water to the main and to the β_{sw} relaxations is more clearly seen in this IPN than in that

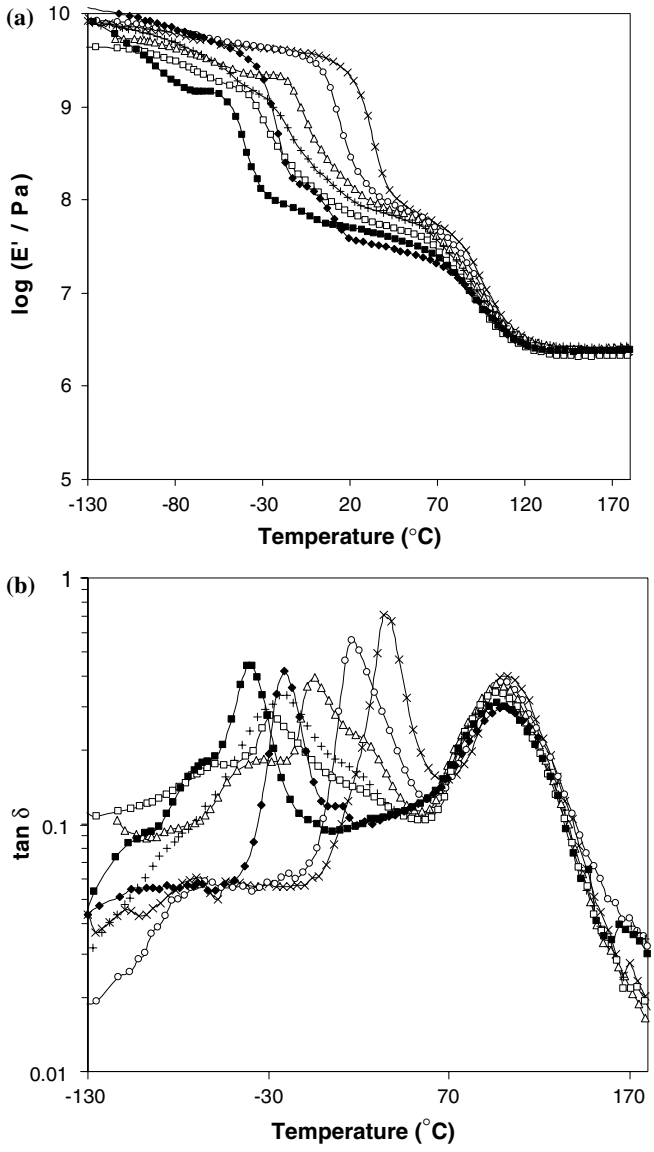

Fig. 4 Temperature dependence of the real part of the elastic modulus (**a**) and the loss tangent (**b**) measured at 1 Hz in the IPN with PHEA mass fraction equal to 0.81 (PEMA sponge synthesized with 60% ethanol and immersed in PHEA monomer) with different water contents: (×) $w = 0.011$, (*open circle*) $w = 0.026$, (*open triangle*) $w = 0.069$, (+) $w = 0.130$, (*open square*) $w = 0.180$, (*filled square*) $w = 0.434$, (*filled diamond*) $w = 0.865$

with lower PHEA mass fractions. The height of the peak increases and the temperature diminishes with increasing water content.

Discussion

Figure 1b shows the equilibrium sorption isotherm of the IPNs when the water content is referred to the mass of PHEA in them, that is $w' = w/x_{\mathrm{PHEA}}$. This plot shows

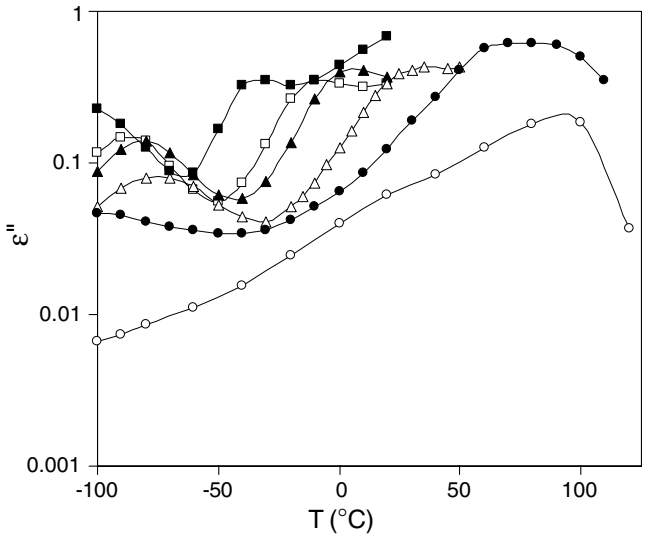

Fig. 5 Imaginary part of the complex dielectric permittivity ε″ measured at 100 Hz in the IPN with PHEA mass fraction equal to 0.15 (PEMA sponge synthesized with 40% ethanol and immersed in the mixture PHEA diluted with 80% of ethanol) with different water contents: (*filled circle*) $w = 0$, (*open triangle*) $w = 0.0074$, (*filled triangle*) $w = 0.0194$, (*open square*) $w = 0.0290$, (*filled square*) $w = 0.0513$. The curve corresponding to the dry pure PEMA network polymerized with 40% ethanol as diluent is also shown for comparison (*open circle*)

that the different experimental isotherms of the IPNs superpose on the isotherm of pure PHEA. This reducibility of the isotherms has been found in other systems [20] and is interpreted to mean that, first, water is sorbed essentially in the hydrophilic phase of the IPNs, and, second, that the behaviour of this phase in the IPNs is that of the pure PHEA homonetwork. In order for this behaviour to be possible, it is necessary to have phase separation, otherwise the behaviour of the hydrophilic phase would not be that of the pure PHEA, due to the hydrophobic interaction with the PEMA chains. In fact as the PEMA network is produced with a porous morphology, the phase separation is expected to happen on a larger scale than in conventional IPNs [11, 20], which means that great hydrophilic domains will exist in the pores of the first network, with a behaviour similar to that of the PHEA network. The reduced curves in Fig. 1b start to diverge for water activities around 0.8: from that activity on the IPNs absorb less water than does the pure PHEA homopolymer. In the PEMA(sponge)-*i*-PHEA IPNs the PHEA phase is confined by a rigid PEMA network, which hinders the PHEA expansion and does not allow the PHEA phase to accommodate the same amounts of water.

The dynamic sorption process in immersion in liquid water is not expected to be a Fickian process due to the great volume increase of the samples during the sorption experiment. Nevertheless, an apparent diffusion

coefficient, D_{ap}, can be calculated according to Fick's diffusion equation in order to characterize numerically the rate of the sorption process in the different IPNs. According to Fick's equation

$$\frac{\partial c}{\partial t} = D_{ap}\frac{\partial^2 c}{\partial x^2},$$

where c is the concentration of water in the sample, x is the distance and t is the time. The solution of this equation in the case of diffusion through a sheet with thickness l for short times corresponding to $\Delta m_t/\Delta m_\infty < 0.6$ (where Δm_t and Δm_∞ are the mass gains of the sample at time t and at equilibrium) can be approximated by [21]

$$\frac{\Delta m_t}{\Delta m_\infty} = 4 \times \left(\frac{D_{ap} \cdot t}{\pi \cdot l^2}\right)^{\frac{1}{2}}. \quad (1)$$

Thus, the plot of $\Delta m_t/\Delta m_\infty$ against $t^{1/2}/l$ must be linear in the initial stage of the sorption process. If K denotes the slope of this linear plot, from Eq. 1

$$D_{ap} = \frac{\pi}{16} \times K^2.$$

Figure 6 shows the apparent diffusion coefficients for the IPNs as a function of the mass fraction of PHEA in them determined by this procedure. Two apparent diffusion coefficients are represented for $x_{PHEA} = 0$; one of them corresponds to the PEMA sponge polymerized with a 40% of ethanol and the other to the PEMA sponge polymerized with a 60% of ethanol. The plot shows a clear increasing tendency of the value of the apparent diffusion coefficient as the mass fraction of PHEA in the IPNs increases. This means that the more hydrophilic the sample, the more rapid is the diffusion process of liquid water in the sample. For PHEA mass fraction lower than 0.4, the apparent diffusion coefficient of the IPNs is lower than that of the corresponding pure PEMA sponge; this means that although these IPNs are more hydrophilic than pure PEMA, the sorption process in immersion in water is slower. This behaviour suggests that the hydrophilic phase in these IPNs is in the form of dispersed domains inside the PEMA sponge, and the loss of continuity of the hydrophilic phase makes the diffusion process more difficult.

As discussed above, the main peak of the TSDC thermograms of the IPNs corresponds to the main relaxation of the PHEA phase in them. The plasticization effect of water is manifested: the temperature of this peak diminishes as the water content of the sample increases. In Fig. 7a the temperature of the α peak of the IPNs is represented as a function of the water content referred to the mass of PHEA in them, $w' = w/x_{PHEA}$. Again, a single reduced curve is obtained, which demonstrates that all hydrophilic phases of the IPNs are

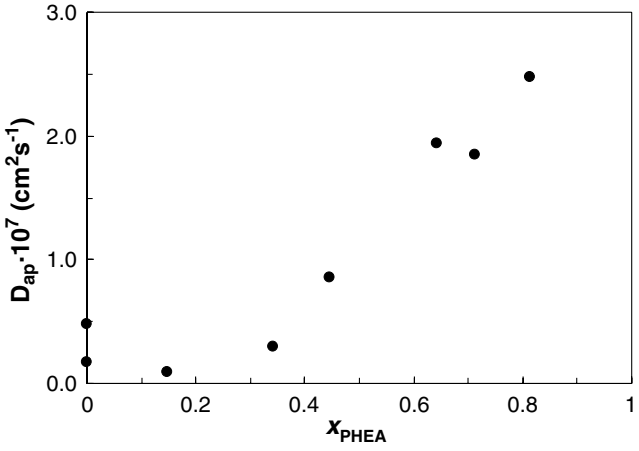

Fig. 6 Apparent diffusion coefficient of water in the IPNs as a function of IPN composition (PHEA mass fraction in it, x_{PHEA}) measured on an immersion experiment. The two points represented at $x_{PHEA} = 0$ correspond to the two types of the PEMA sponges

equally plasticized. This result supports the hypothesis that the system is a phase-separated one in which water is mainly absorbed by the hydrophilic phase in it.

The same conclusion can be reached from the dynamic-mechanical results obtained with samples with a water content below 0.3 g of water per gram of PHEA, as shown in Fig. 7b. Further amounts of water do not contribute to the plasticization of the PHEA chains. Differential scanning calorimetry (DSC) experiments [16, 22, 23] show that in pure PHEA network above this water content, a crystallization peak appears in cooling scans. Thus, at the beginning of the DMS measuring scan, the samples with $w' \geq 0.3$ contain nanometric pure solid water domains dispersed in the polymer matrix. At temperatures below 0 °C these domains are in the solid phase and act as a reinforcing disperse filler from the mechanical point of view, whose effect is to shift the glass transition to higher temperatures and to increase the elastic modulus. Immediately before the drop of E' in the main transition, the value corresponding to the sample containing solid water domains can be up to five times the modulus of the sample with a water content around $w' = 0.3$. This result strongly supports the conclusions of the DSC experiments on the phase diagram of the PHEA-water system [16, 22, 23]. By comparing the TSDC and the DMS results with each other (Fig. 7a, b) it is interesting to note the shift of the DMS data to higher temperatures due to the higher frequency of measurements (1 Hz against about 1 mHz [13, 14]). However, the range of temperature shift due to plasticization is the same by both techniques, as it should be expected, approximately 90 °C.

The secondary relaxations of PHEA and their evolution with increasing water content in the network have been explained elsewhere [11, 13, 19]. The same

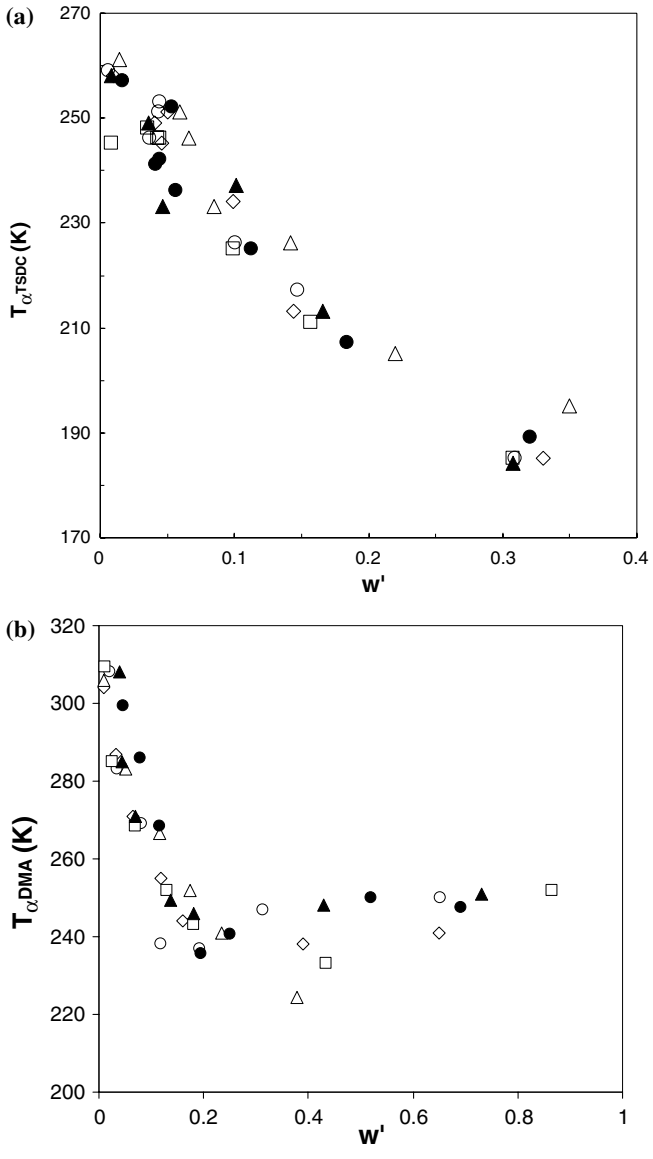

Fig. 7 Temperature of the TSDC peak (**a**) and DMS loss tangent peak (**b**) corresponding to the main relaxation of PHEA, α, as a function of water content of the hydrogel referred to PHEA weight in the sample, w'. The samples are identified by their PHEA mass fraction equal to: 0.81 (*open square*), 0.71 (*open diamond*), 0.64 (*filled triangle*), 0.45 (*open circle*), 0.34 (*filled circle*), 0.15 (*open triangle*)

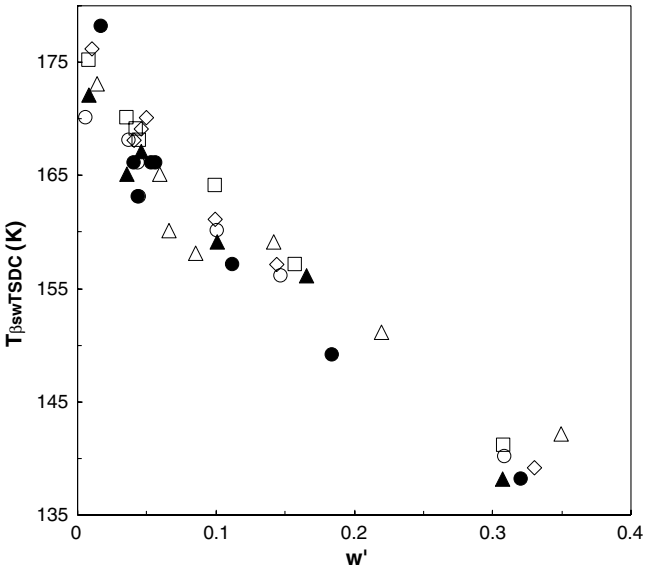

Fig. 8 Temperature of the TSDC peak corresponding to the β_{sw} secondary relaxation of the PHEA phase in the IPNs as a function of water content of the hydrogel referred to PHEA weight in the sample, w'. The samples are identified by their PHEA mass fraction equal to: 0.81 (*open square*), 0.71 (*open diamond*), 0.64 (*filled triangle*), 0.45 (*open circle*), 0.34 (*filled circle*), 0.15 (*open triangle*)

behaviour is found here for the hydrophilic phase of the PEMA(sponge)-*i*-PHEA IPNs. The temperature of the γ relaxation is not affected by water content; this relaxation is due to internal motions in the $-CH_2-CH_2-OH$ groups and shows up as long as there remain such groups free from association with water molecules. The incorporation of water into the PHEA phase leads to the occurrence of a new relaxation, labeled β_{sw}, which was interpreted in the literature, is due to the motion of a new lateral group formed by the association of one water molecule and two side-chain hydroxyl groups [16, 17, 19, 24]. As shown in Fig. 3, a rapid increase of the magnitude of the β_{sw} relaxation is observed at low water contents, when the water molecules are mainly at the first sorption layer of the polymer. As it is only the first sorbed water molecules that can associate with the hydroxyl groups, consequently, a slower increase is observed for higher water fractions. The increase of the number of water molecules is probably accompanied by a weakening of interactions between lateral chains, which would thus confer more mobility to the relaxational unit, shifting the temperature of the β_{sw} relaxation towards lower values. Figure 8 shows the evolution of the temperature of this peak in all the IPNs as a function of the water content referred to the mass of PHEA in them, w'. Once again a reduced single curve is observed for all IPNs, which supports the hypothesis that the behaviour of the hydrophilic phase in the IPNs is not affected by the presence of the hydrophobic phase.

If the PHEA phase behaviour of the IPNs is not affected by the presence of the PEMA sponge when the water activity of the samples is lower than one, a different situation shows up when the samples are equilibrated in immersion in liquid water. The importance of the morphology of the PEMA sponge on the sorption capacity and expansion of the hydrophilic phase can be remarked in these experiments. Figure 9 shows the equilibrium water content of the IPNs referred to the PHEA phase when immersed in liquid water, w'^{**}, compared with that of pure PHEA when immersed in

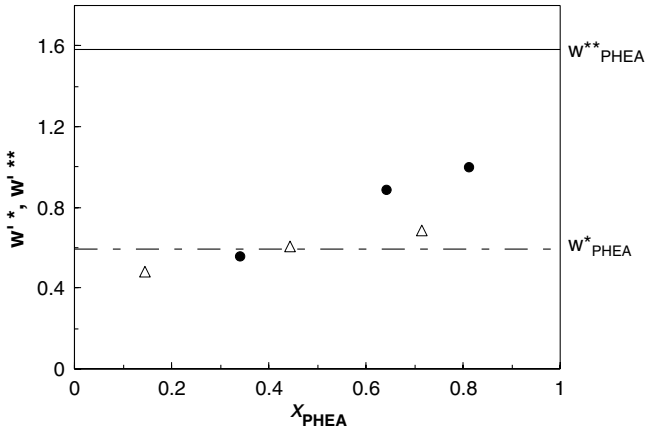

Fig. 9 Equilibrium water content of the PHEA phase in the IPNs in immersion in liquid water, w'^{**}, as a function of their mass fraction of PHEA, x_{PHEA}. The symbols represent: (*filled circle*) a series of IPNs whose PEMA first network was polymerized with a 60% of ethanol and (*open triangle*) a series of IPNs whose PEMA first network was polymerized with a 40% of ethanol. The horizontal lines represent the equilibrium sorption of pure PHEA network by immersion in liquid water (w^{**}_{PHEA}) and in saturated vapour (w^{*}_{PHEA})

liquid water, w^{**}_{PHEA}, and in equilibrium in a saturated vapour, w^{*}_{PHEA} (dotted lines). The difference found for w^{*}_{PHEA} and w^{**}_{PHEA} for the same value of water activity has been explained elsewhere [25]. The first value corresponds to saturation of the gel with its micelles or collapsed heterogeneities unavailable for sorption because the expansion of the network is insufficient to open and disentangle those structures. The second value corresponds to saturation of the gel in a state where those structures have loosened and opened, and the network can lodge a pure water phase in it because the elastic energy of network expansion in immersion in liquid water is enough to produce this effect. For IPN composition lower than $x_{PHEA} < 0.5$, the PHEA network is thought to be dispersed in the PEMA sponge, and its water sorption capacity in immersion does not exceed the water content in saturated vapour equilibrium of the homonetwork. When $x_{PHEA} > 0.5$ both phases (hydrophilic and hydrophobic) are thought to be cocontinuous, but, there exists a clear difference between the behaviour of the samples where the PEMA sponge is prepared with a 60% of ethanol and those synthesized with a 40% of ethanol. In the former the equilibrium water content in immersion is higher than that of pure PHEA in equilibrium in saturated vapour, which means that the PHEA phase in the IPNs can expand to some extent, micellized chain segments and micropores can open and a liquid water phase can be lodged in the hydrogel phase. This means that the expansion of the network has been able to overcome the confining effect of the PEMA sponge. This situation is only possible if the PEMA sponge is formed by a loosely connected structure of merged microspheres; in the presence of this morphology, the expansion of the PHEA phase can distort the PEMA sponge and expand. When the amount of diluent used in the polymerization of the PEMA sponge is only 40%, the expansion of the PHEA network is quite small, since the water content in immersion is similar to that of pure PHEA in equilibrium in saturated vapour. This suggests that the morphology of the PEMA sponges is similar to a honeycomb-like structure, as found also in other systems [26], which is much more rigid and prevents the expansion of the hydrophilic phase to some extent. This structural difference can also be related with the spectra of the dynamic-mechanical measurements for the pure PEMA sponges (results not shown). Indeed the rubber mechanical storage modulus for the PEMA sponge polymerized with a 60% of ethanol is lower than that for the sample prepared with a 40% of ethanol. Also the magnitude of tan δ for the most porous sponge is higher after the main relaxation due to an additional friction mechanism when the pores are opened [26].

Conclusions

The PEMA(sponge)-*i*-PHEA IPNs are phase-separated systems as revealed by the reducibility of the equilibrium sorption isotherms when the water content is referred to the PHEA mass fraction in them. The existence of this 'universal' sorption isotherm means that water is sorbed essentially in the hydrophilic phase of the IPNs, and the behaviour of this phase in the IPNs is similar to that of the pure PHEA homonetwork. However, in equilibrium in a vapour environment at the highest water activities, a confining effect of the PEMA network is manifested, and the water content of the hydrophilic phase in the IPNs is lower than in the pure hydrophilic homonetwork. The increasing tendency of the value of the apparent diffusion coefficient as the mass fraction of PHEA in the IPNs increases shows that the more hydrophilic the material the more rapid is the diffusion process of liquid water in the sample. For PHEA mass fraction lower than 0.4, the hydrophilic phase in the IPNs forms disperse domains inside the PEMA sponge as revealed by the lower diffusion coefficients compared to that of the PEMA homonetwork. The evolution of the temperature of the main relaxation, measured by TSDC and DMS, of all IPNs as a function of the water content in the sample referred to the mass fraction of PHEA in them also reduces to a single curve, which confirms the biphasic nature of the IPNs. DMS measurements show that the samples with $w' \geq 0.3$ contain nanometric pure solid water domains (crystallized at temperatures below 0 °C) that act as a reinforcing dispersed filler from the mechanical point of view, whose effect is to shift the glass transition to higher temperatures and to increase the elastic modulus. When the samples are equilibrated

in immersion in liquid water, the importance of the morphology of the PEMA sponge on the sorption capacity and expansion of the hydrophilic phase can be remarked. For IPN composition lower than $x_{PHEA} < 0.5$, the PHEA network is dispersed in the PEMA sponge, and its water sorption capacity in immersion does not exceed the water content in saturated vapour equilibrium of the homonetwork. When $x_{PHEA} > 0.5$ both phases (hydrophilic and hydrophobic) are thought to be cocontinuous, but there is a clear difference between the behaviour of the samples where the PEMA sponge is prepared with a 60% of ethanol and those synthesized with a 40% of ethanol. In the former, the PEMA sponge is formed by a connected set of merged microspheres, and the PHEA phase in the IPNs can expand to some extent and overcome the confining effect of the PEMA. When the amount of diluent used in the polymerization of the PEMA sponge is 40%, the morphology of the PEMA sponges is more similar to a honeycomb-like structure, and the expansion of the PHEA network is almost the same as the expansion of the PHEA homonetwork when equilibrated in saturated vapour.

Acknowledgements This work was supported by the Generalitat Valenciana through project CTIDIA/2002/046 and by NTUA through the programme Thales.

References

1. Tsuruta T (1996) Adv Polym Sci 126:1
2. Hoffman AS (2002) Adv Drug Deliv Rev 43:3
3. Kazanskii KS, Dubrovskii SA (1992) Adv Polym Sci 104:97
4. Klempner D, Sperling LH, Utracki LA (1994) Interpenetrating polymer networks, Adv Chem Ser 239. American Chemical Society, Washington
5. Stoy V, Kliment C (1996) Hydrogels: speciality plastics for biomedical and pharmaceutical applications. Technomic Pu, Basel
6. Roh HW, Song MJ, Han DK, Lee DS, Ahn JH, Kim SC (1999) Biomater Sci, Polym Ed 10:123
7. Donatelli AA, Sperling LH, Thomas DA (1976) Macromolecules 9:671
8. Salmerón M, Gallego Ferrer G, Torregrosa Cabanilles C, Meseguer Dueñas JM, Monleón Pradas M, Gómez Ribelles JL (2001) Polymer 42:10071
9. Eschbach FO, Huang SJ (1994) In: Klempner D, Sperling LH, Utracki LA (eds) Interpenetrating polymer networks, Adv Chem Ser 239. American Chemical Society, Washington, p 205
10. Kim SJ, Lee KJ, Kim IY, An KH, Kim SI (2003) J Appl Polym Sci 90:1384
11. Gómez Ribelles JL, Monleón Pradas M, Gallego Ferrer G, Peidro Torres N, Pérez Giménez V, Pissis P, Kyritsis A (1999) J Polym Sci B Polym Phys 37:1587
12. Greenspan L (1977) J Res Nat Bur Stand (US) 81A:89
13. Kyritsis A, Pissis P, Gómez Ribelles JL, Monleón Pradas M (1994) J Polym Sci B Polym Phys 32:1001
14. Sessler GM (1980) Electrets. Topics in Applied Physics, vol 33. Springer, Berlin Heidelberg New York
15. Adamson AW (1990) Physical chemistry of surfaces, 5th edn. Wiley, New York
16. Kyritsis A, Pissis P, Gómez Ribelles JL, Monleón Pradas M (1994) J Non-Cryst Solids 172–174:1041
17. Janáček J, Kolařík J (1965) Collect Czech Chem Commun 30:1507
18. Bareš J, Janáček J (1965) Collect Czech Chem Commun 30:1604
19. Gómez Ribelles JL, Meseguer Dueñas JM, Monleón Pradas M (1988) Polymer 29:1124
20. Gallego Ferrer G, Monleón Pradas M, Gómez Ribelles JL, Pissis P (1998) J Non-Cryst Solids 235–237:692
21. Crank J, Parks GS (1968) Diffusion in polymers. Academic, London
22. Rault J, Lucas A, Neffati R, Monleón Pradas M (1997) Macromolecules 30:7866
23. Salmerón Sánchez M, Gallego Ferrer G, Monleón Pradas M, Gómez Ribelles JL (2003) Macromolecules 36:860
24. Kolařík J (1982) Adv Polym Sci 46:119
25. Gallego Ferrer G, Monleón Pradas M, Gómez Ribelles JL, Salmerón Sánchez M (2004) Polymer (in press)
26. Monleón Pradas M, Gómez Ribelles JL, Serrano Aroca A, Gallego Ferrer G, Suay Antón J, Pissis P (2001) Polymer 42:4667