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Water sorption of flexible networks based on 2-hydroxyethyl methacrylate–triethylenglycol dimethacrylate copolymers

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Cross-linked films of copolymers of 2-hydroxyethyl methacrylate (HEMA) and triethylenglycol dimethacrylate (TEGDMA) were prepared by free radical polymerization initiated at 60°C. The swelling behaviour of films prepared with 2, 5 and 10 mol% of TEGDMA was followed gravimetrically and the diffusion coefficients were determined according to the Fickian law at several temperatures in the interval 25–50°C. The apparent activation energy was independent of the composition of the networks, giving a value of 15.5 kJ mol^{-1} which corresponds to a typical diffusion process. The freezing point, the enthalpy of fusion and the amount of non-freezable water were determined by differential scanning calorimetry (DSC) on hydrated samples with different hydration degree. There is a critical hydration interval ($W = 20$–30 wt%) in which it is possible to distinguish the different states of water in the cross-linked hydrogel. The variation of the enthalpy ΔH_f with the hydration degree gives a maximum amount of non-freezable water of about 23 wt%, independent of the TEGDMA content of copolymer systems. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Hydogels are hydrophilic polymer networks which have a high capacity to adsorb a substantial amount of water, which are characterized by the presence of cross-links, crystalline and amorphous regions, entanglements and rearrangement of hydrophobic/hydrophilic domains[1–3]. Hydrophilic cross-linked and uncross-linked gels are of special interest in biological environments because they have a high water content, similar to that of several body tissues, and can be easily prepared without dangerous impurities[4–6]. Poly(hydroxyethyl methacrylate)-based hydrogels have been widely studied and applied in different biomedical specialities, because of their swelling behaviour and chemical stability. In addition to their good biocompatibility it is possible to modify their elasticity by changing the network structure and cross-linking density, by the addition of small amounts of cross-linking agents[6–10]. One of the most interesting biomedical applications of this kind of hydrogels is the preparation of soft contact lenses, based on lightly cross-linked combinations of HEMA with vinyl pyrrolidone, methyl methacrylate, glycidyl methacrylate, etc., the most common cross-linking agent being ethylenglycol dimethacrylate[11].

The water adsorption characteristics of hydrogels have a significant influence on the diffusive behaviour of small molecules through the gel, the interfacial interactions, etc.[12] In this sense, the interactions and the thermodynamic characteristics of water in hydrogels have been extensively studied by Andrade[13], McBrierty and coworkers[14,15] and Pedley and Tighe[16]. Using different analytical techniques these authors have described three different states of water in the hydrogel matrix, according to the bound water associated with the polymer chains and networks, and the non-bound water. The non-bound water provides different energetic states depending on the associating strength of the water–water and water–polymer interactions. Pedley and Tighe[16] studied three states of water in styrene/HEMA random copolymers with the assumption that the HEMA sequences were clustered in microdomains interacting specifically with water molecules. The cross-linking density was found to have a great influence on the mechanical strength and swelling capacity of hydrophilic poly(acrylic systems)[17].

In the present work relatively high cross-linked systems obtained by the free radical copolymerization of HEMA with a very flexible cross-linking agent, triethylenglycol dimethacrylate, are studied. The swelling behaviour and the state of water in the hydrogels are analysed on the basis of diffusion theories and thermodynamic characteristics of the network with a relatively high cross-linking density, according to the composition of the copolymers prepared.

EXPERIMENTAL

Monomer preparation and purification of materials

2-Hydroxyethyl methacrylate, supplied by Hydron Europe Ltd., containing less than 0.05 wt% of ethylene

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glycol dimethacrylate, was distilled under reduced pressure of nitrogen and the fraction of BP 87–89°C/5 mm Hg was collected. Triethylene glycol dimethacrylate (Fluka) was used as received. 2,2'Asobisisobutyronitrile (AIBN) was purified by fractional crystallization from methanol (MP 104°C).

Polymerization procedure

2-Hydroxyethyl methacrylate (HEMA) and triethylene glycol dimethacrylate (TEGDMA) were mixed in selected proportions and AIBN was added as an initiator (1 wt%). The reacting mixture was de-aired with nitrogen and poured into a cylindrical teflon mould (30 mm diameter and 5 mm deep).The covered teflon mould was placed in an oven with accurate temperature control, and the polymerization was carried out for 24 h at 60°C. Once the reaction was complete a transparent and rigid polymer membrane was obtained which could be easily separated from the teflon disk mould. The thickness was accurately measured with a high-precision micrometer.

Swelling experiments

The membranes were cut into fragments of about 120–150 mg and weighed accurately. These fragments were placed into a flask with 10 ml of distilled water and kept in a water-thermostated bath at the desired temperature. The water uptake, W, was calculated by measuring the weight gain of the sample at different times after carefully wiping the surface with a filter paper. It was reported as

$$W = (M - M_0)/M_0 = M/M_0 - 1 \qquad (1)$$

where M_0 is the weight of the dry sample and M is that of the sample at time t.

Differential scanning calorimetry (DSC)

The measurements were preformed with a Perkin-Elmer, DSC-4 calorimeter interfaced to a thermal analysis data system. A slice of the water-swollen membrane (~10–20 mg) was placed in the aluminium pan, cooled with liquid nitrogen to −60°C, and then heated at 5°C min^{-1} to 50°C. The water content was varied by standing the membrane at room temperature for a given period in order to evaporate water. After the appropriate weight of the sample was reached, the gel was covered with a film of teflon for at least 24 h in order to reequilibrate the system, and kept in a closed box at 25°C. This guaranteed the homogeneous distribution of water molecules in the gel.

RESULTS AND DISCUSSION

Swelling experiments

HEMA/TEGDMA copolymers were prepared by the thermally initiated free radical polymerization of HEMA,

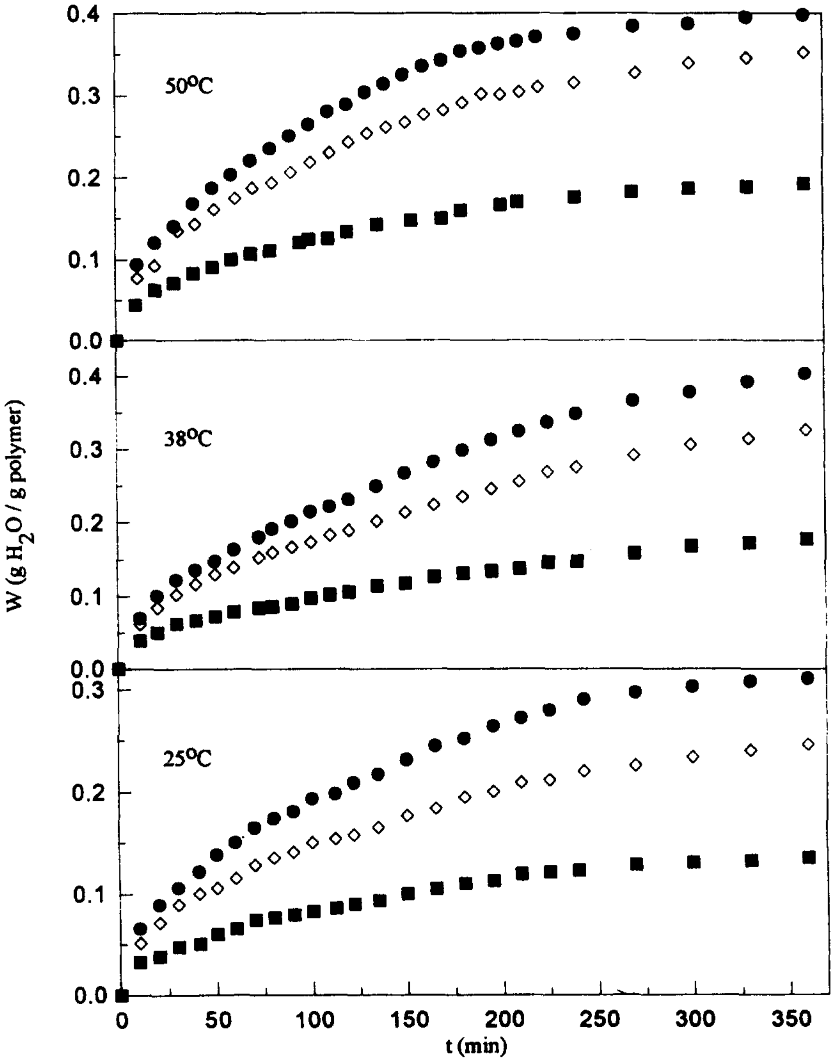

Figure 1 Sorption isotherms for HEMA/TEGDMA copolymers at 25, 38 and 50°C. (●) 2, (◇) 5 and (■) 10 mol% of TEGDMA in the copolymer

Table 1 Values of the equilibrium water content W_∞, and diffusion constant, D, for the HEMA/TEGDMA copolymers at 25, 38 and 50°C

Content of TEGDMA (mol%)	$W\infty$ (g H_2O/g of polymer)			$D \times 10^7$ ($cm^2 s^{-1}$)		
	25°C	38°C	50°C	25°C	38°C	50°C
2	0.4750	0.438	0.4030	2.87	4.49	7.49
5	0.3896	0.3580	0.3447	2.75	4.62	7.53
10	0.2898	0.2806	0.2728	1.98	2.99	5.05

with different amounts of the tetrafunctional monomer TEGDMA, namely 2, 5 and 10 mol%. The copolymerization reaction was carried out in bulk at 60°C, using AIBN as an initiator. The polymer films obtained were transparent and stiff, with glass transition temperatures ranging from 50 to 60°C, depending on the copolymer composition. After immersion in water, the films readily swelled in an extension that depended on the composition of the film and the temperature of the experiment.

Figure 1 shows the variation of the water uptake (W) at three temperatures as a function of the swelling time for three HEMA/TEGDMA copolymers. As can be observed, there is a strong dependence of the water uptake on composition, which is reflected in the equilibrium water uptake, after 24 h of treatment, W_∞, reported in *Table 1*. The swelling of cross-linked polymers is the result of a compromise between the osmotic swelling pressure and the elastic force of the macromolecular chains of the network opposing it. Therefore, as the composition of the HEMA/TEGDMA copolymer becomes richer in TEGDMA, the water uptake decreases. After the swelling experiments, the films were dried at room temperature, under a high vacuum until constant weight was attained. In all cases the difference of the dry films with respect to the original sample was less than 1.0 wt%, even for the networks prepared with the lowest concentration of the tetrafunctional cross-linking agent, TEGDMA. This means that no hydrosoluble polymer is produced in the experimental conditions used in the present work.

It is interesting to point out that the values of the equilibrium water content shown in *Table 1* are in very good agreement with those recently reported for polyHEMA membranes cross-linked with 1, 6-hexamethylene diisocianate (HMD)[18]. The equilibrium water content at 25°C for the polyHEMA membranes ranged from 39.7 wt% for the sample with 1.0 mol% of HMD to 43.8 wt% for the sample with 0.5 mol% of HMD.

The penetration of a solvent into a stiff polymer sample is usually described as the result of two different processes: the diffusion of the solvent into the swollen matrix, and the advancement of the swollen–unswollen boundary as a consequence of the stress induced in the polymer[19]. When the rate-determining step is the first mechanism, there is a linear dependence between the solvent uptake and $t^{1/2}$, and the system is said to exhibit a Fickian behaviour. In contrast, if the advancement of the swollen–unswollen boundary is slower than the diffusion of the solvent in the swollen polymer, zero- order kinetics are observed and the water uptake increases linearly with the swelling time.

Figure 2 shows the water uptake *versus* $t^{1/2}$ diagrams obtained at 38°C with the HEMA/TEGDMA copolymer films for the three compositions studied. It can be appreciated that Fickian behaviour is obeyed up to approximately 200 min of swelling, although for longer times the behaviour deviates from the linearity. The same pattern was obtained for the experiments preformed at 25 and 50°C.

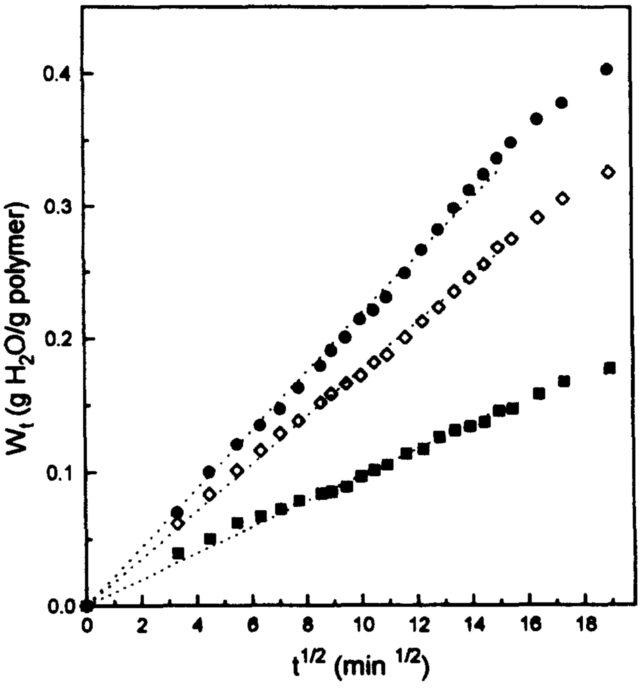

Figure 2 Water uptake as a function of $t^{1/2}$ for HEMA/TEGDMA copolymers with different composition. Symbols have the same meaning as in *Figure 1*

The solution of the differential form of Fick's law for thin sheets neglecting diffusion through the edges, can be expressed as a function of the reduced uptake M_t/M_∞ (or W_t/W_∞) and $t^{1/2}$ according to the following relationship[20]:

$$M_t/M_\infty = 4[D_t/\pi l^2]^{1/2} = W_t/W_\infty \qquad (2)$$

where M_t and M_∞ represents the water uptake at time t and infinite, respectively, D is the difussion coefficient and l is the average thickness of the film.

From the straight lines of the W_t *versus* $t^{1/2}$ plots, and taking into consideration the value of W_∞ reported in *Table 1* and the thickness of the film, the diffusion coefficient of copolymers were determined. The values obtained are reported in *Table 1*. It can be seen that there is no noticeable difference in the diffusion coefficients of copolymers with 2 and 5 mol% of TEGDMA, but the copolymer with 10 mol% of TEGDMA exhibits a smaller value of D owing to the greater cross-linked structure of the latter.

The temperature dependence of the diffusion coefficients obtained was analysed on the basis on an Arrhenius-type equation:

$$D = D_0 \exp(-E_D/RT) \qquad (3)$$

where E_D is the apparent activation energy for the diffusion process. As shown in *Figure 3*, the expected linear dependence of the logarithm of D on $1/T$ was obtained. From the slopes of the straight lines in *Figure 3*, an average activation energy of $E_D = 15.5$ kJ mol^{-1} was determined. This value is

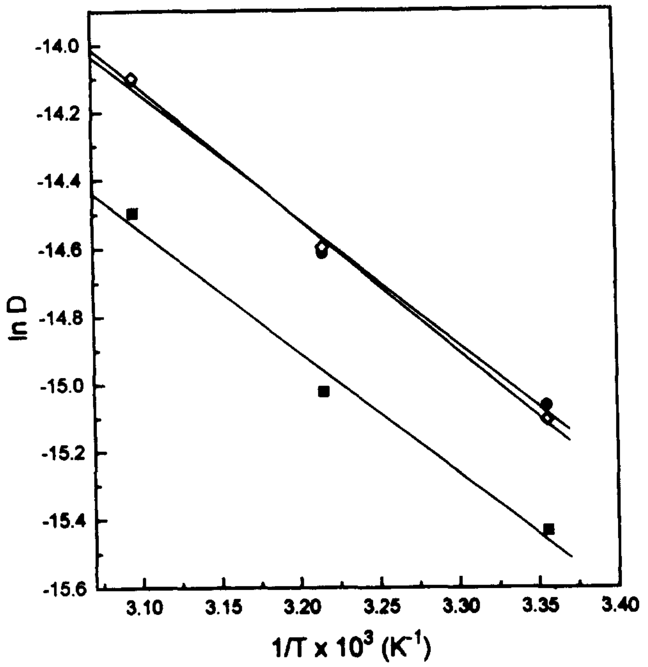

Figure 3 Temperature dependence of the diffusion coefficient, D, for the HEMA/TEGDMA copolymers with a different composition. Symbols have the same meaning as in *Figure 1*

in the interval of typical diffusion process of water in hydrophilic polymer systems[2].

It can be appreciated in *Figure 2* that for long swelling times the experimental points seem to deviate from the Fickian behaviour, characterized by the straight lines of the W *versus* $t^{1/2}$ plots. For extensive swelling of polymers, Schott[21] proposed an expression of the form:

$$t/W = A + B.t \tag{4}$$

where W if the water uptake at time t, $B = 1/W_\infty$, the inverse of the maximum swelling and $A = 1/(\mathrm{d}W/\mathrm{d}t)_0$, the reciprocal of the initial swelling rate. In fact, Schott demonstrated that equation (4) implies a second-order swelling kinetics.

The diagrams obtained by the application of equation (4) to the data in *Figure 1* give straight lines straight with excellent correlation coefficients, as is illustrated in *Figure 4* for the swelling data obtained at 38°C. The same pattern was obtained for the data at 25 and 50°C.

An interesting feature of the system studied is the temperature dependence of W_∞, the equilibrium water uptake of the HEMA/TEGDMA copolymers. W_∞ is plotted against the reciprocal of the swelling temperature in *Figure 5*. Straight lines with positive slopes are obtained for the three compositions studied. This behaviour can be analysed taking into consideration the Gibbs–Helmholtz equation for the infinite or equilibrium water content[12]:

$$\frac{\mathrm{d}\ln(W_\infty)}{\mathrm{d}(1/T)} = -\frac{\Delta H_\mathrm{m}}{\mathrm{R}} \tag{5}$$

where R is the gas constant and ΔH_m is the enthalpy of mixing between the dry polymer and an infinite amount of water. The positive slope of the lines in *Figure 5* indicates an exothermic mixing process. Using equation (5) the values of ΔH_m were obtained. They are listed in *Table 2*, where it can be appreciated that the absolute values of ΔH_m are quite small, but they exhibit a considerable dependence on the copolymer composition.

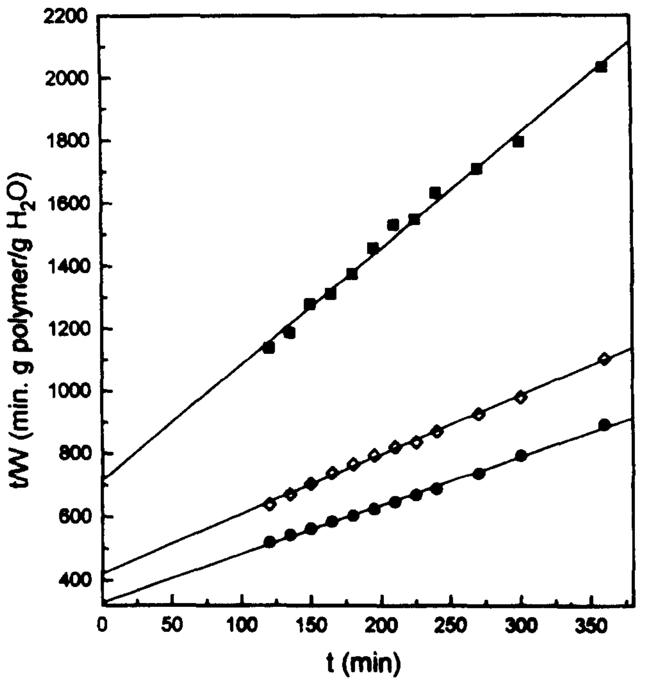

Figure 4 Reciprocal of the average swelling rate t/W, as a function of the time of treatment. Straight lines correspond to the least-squares fit of experimental points to equation (4). Symbols have the same meaning as in *Figure 1*

Table 2 Values of the apparent activation energies for diffusion, E_D, and the enthalpy of mixing ΔH_m, for the HEMA/TEGDMA copolymers

Content of TEGDMA (mol%)	E_D (KJ mol^{-1})	ΔH_m (KJ mol^{-1})
2	15.4	−2.7
5	16.2	−2.0
10	15.0	−1.0

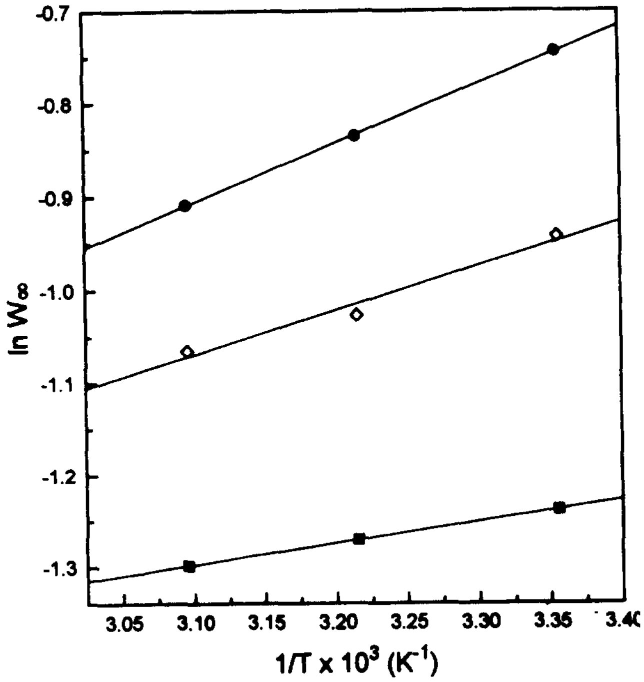

Figure 5 Temperature dependence of the equilibrium water content, W_∞, for HEMA/TEGDMA copolymers. Symbols have the same meaning as in *Figure 1*

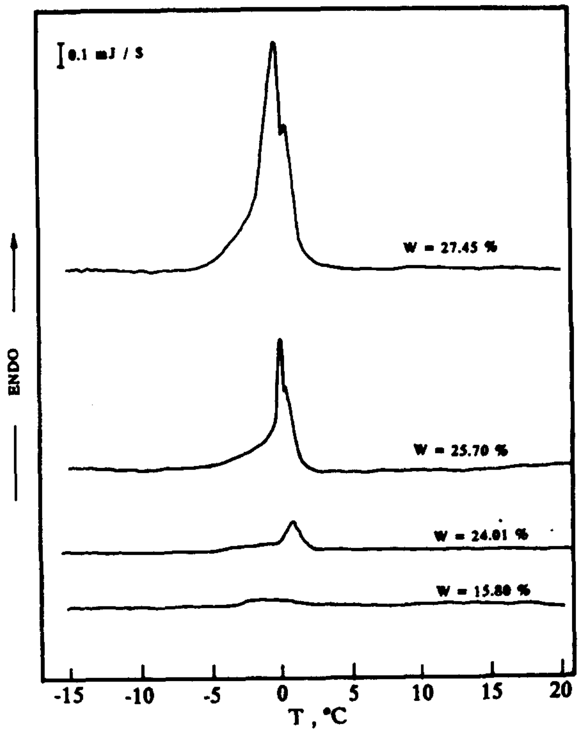

Figure 6 DSC thermograms for the HEMA/TEGDMA copolymer with 10 mol% of TEGDMA with different water content as indicated in the diagram

DSC experiments

Differential scanning calorimetry has proved to be very useful in determining the state of water in hydrogels (see for example Ref. [22]). It allows one to differentiate between the non-freezing water (the water that is more tightly bound to the polymer), and the freezing or more loosely bound and free water. Moreover, from the pattern of the melting peaks of freezing water it is sometimes possible to discriminate the proportion of the free or unbound freezing water from the freezing water that is more loosely bound to the polymer.

Figure 6 shows the DSC thermograms of polymer films prepared with a 10 mol% of TEGDMA, at swelling degrees. The thermograms were recorded in the experimental conditions outlined in the experimental section, after quenching of the hydrated films at −60°C in the calorimeter for 30 min. The analysis of the endothermic transition associated to the melting of the frozen water makes clear the different behaviour in relation to the water–polymer interactions. There is a critical hydration interval (W = 20–30 wt%) in which it is possible to distinguish the different states of the water in the cross-linked hydrogel. In fact, for a hydration degree of $W = 15.80$ wt% no peak of melting of frozen water is detected, and only a very smooth and broad deviation from the base line could be observed. A broad exotherm has been described for polyHEMA hydrogels, which has been associated to a devitrification of part of the glassy or tightly bound water[14,23,24]. This indicates that water is completely associated to the copolymer network without any crystallization. The most interesting changes in the thermograms are observed in a very narrow interval of hydration, which corresponds to swelling degrees between 24 and 28 wt%. The thermogram obtained for hydrated samples with a $W = 24.01$ wt% shows a small and relatively broad endothermic peak, with the maximum centred at 0.98°C, together with the smooth deviation observed in the sample with 15.80 wt%. The thermograms of more hydrated films present a sharp endothermic peak at 0.10–0.15°C associated to the melting of pure crystallized water, but a shoulder at 0.95–1.00°C remains for these compositions. This shoulder disappears for films with hydration degrees higher than 30 wt%. The most important consequence of these results is that the DSC demonstrates the existence of non-freezable and frozen water in the cross-linked hydrogels as a consequence of the polar interactions between the water molecules and functional groups of the macromolecular network. In addition, there is a transition state between the non-freezing and frozen states in which crystallization of water is possible but with the interaction of the polymeric segments of the network, which is probably responsible for the melting endotherm at a slightly higher temperature (0.95–1.00°C).

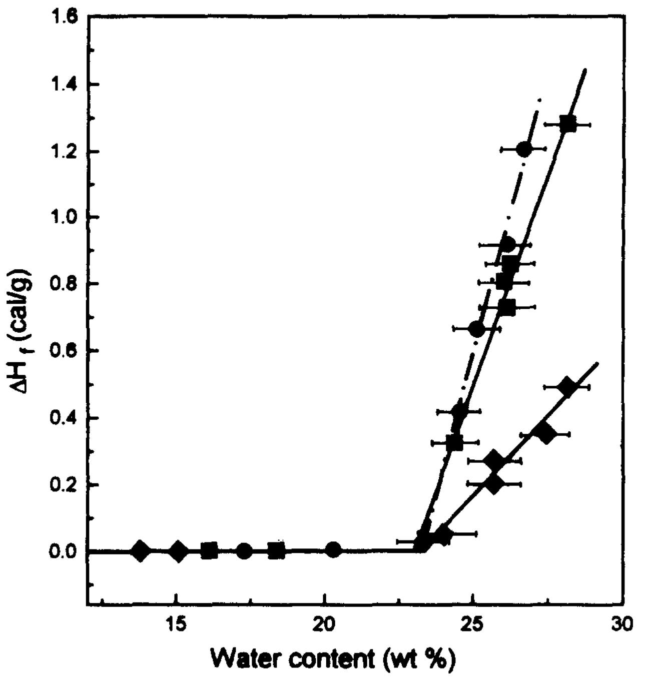

Figure 7 Plot of the heat of fusion, ΔH_f, as a function of the water content for HEMA/TEGDMA copolymers with 2 (•), 5 (■) and 10 (♦) mol% of TEGDMA. Both ΔH_f and water content are related to the dry polymer

The integrated change of enthalpy ΔH_f (per gram of dry polymer) as a function of the water content for copolymers with 5 and 10 mol% of TEGDMA is shown in *Figure 7*. From the extrapolation of the straight lines to $\Delta H_f = 0$ the maximum amount of non-freezable water was obtained. This was found to be 23 ± 4 wt% for both samples, which coincides within the experimental error with the value of 25 ± 4 wt% reported for polyHEMA in experiments carried out at the same scanning rate[14]. The systems prepared with 2 and 5 mol% of TEGDMA gave straight lines with a higher slope than that of the system with 10 mol% of the cross-linked monomer, but the trend is very similar to that reported by Quinn *et al.* for polyHEMA[14]. Although it is very difficult to predict the complex behaviour of water in the proximity of 0°C, it seems to be clear that there is a critical maximum concentration of bound water which does not depend on the average composition in the interval studied in this work. For hydration degrees above the critical point (23 ± 4 wt%), the percentage of TEGDMA in the copolymer systems appears to influence the quantity of freezable water which is clearly lower for the system with 10 mol% of TEGDMA. This behaviour can be the result of the relatively high cross-linking density in addition to the relative increase of oxyethylene groups (three per TEGDMA molecule), which could interact with the water molecules through hydrogen bonding.

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