Polymeric Hydrophilic Hydrogels with Flexible Hydrophobic Chains. Control of the Hydration and Interactions with Water Molecules

Blanca Vázquez and Julio San Roman*

Instituto de Ciencia y Tecnologia de Polimeros, CSIC, Juan de la Cierva, 28006-Madrid, Spain

Carlos Peniche and M. Eugenia Cohen

Centro de Biomateriales, Universidad de la Habana, 10400-Havana, Cuba

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ABSTRACT: Acrylic hydrogels based on 2-hydroxyethyl methacrylate, H, have been synthesized by copolymerization reaction of this monomer with 2-ethylhexyl acrylate, E, using AIBN as initiator. Reactivity ratios were estimated from copolymerization reactions carried out in solution and at low conversion, by using both linearization and nonlinearization methods. They were found to be $r_E = 0.29$ and $r_H = 2.54$. The swelling behavior of the hydrogels was studied by immersion of copolymer films prepared by bulk copolymerization, in water at different temperatures. Equilibrium water uptake was strongly dependent on composition and decreased with the E content in the copolymer. Fickian behavior was observed in all cases for reduced sorption coefficients lower than 0.4. The diffusion coefficient was found to decrease with increasing E content in the copolymer. A value of apparent activation energy for the diffusion process of 8.8 kJ/mol was obtained for poly(2-hydroxyethyl methacrylate); however, H/E copolymers did not obey the Arrhenius behavior over the short temperature interval studied. Differential scanning calorimetry has been used to study the organization of water in the copolymer hydrogels. The amounts of nonfreezable water for the copolymers with 5 and 10 wt % of E content were found to be 28 and 26 wt %, respectively. The surfaces of the copolymer films were characterized by contact angle measurements. The surface free energy decreased noticeably with the presence of 10 wt % of the flexible hydrophobic monomer, the reduction of the polar component being higher than that of the dispersive component. Segregation of the components in microdomains, the H segments being the continuous phase, is postulated tentatively in the light of the results obtained.

Introduction

2-Hydroxyethyl methacrylate based hydrogels prepared by free radical polymerization or copolymerization with other acrylic or vinyl monomers have been largely employed in biomedical applications such as soft contact lenses,[1] wound dressings,[2] blood compatible surfaces,[3,4] drug release systems,[5,6] surgical prostheses,[7] etc. In copolymeric systems the swelling process is controlled by the introduction of the appropriate amount of a second monomer with hydrophobic character. The maximum hydration degree and diffusion of the swelling agent into the gel, as well as the organization of water molecules in the gel, will change depending on the chemical composition and the distribution of the hydrophobic monomeric units along the macromolecular chains.[8,9] New trends in the field of contact lenses are directed to the preparation of systems with hydrophobic microdomains of smaller size than the light wavelength in order to prepare devices with improved permeability for oxygen without a drastic loss of the good transparency and optical properties of poly(hydroxyethyl methacrylate)-based polymeric formulations. Differential scanning calorimetry has been widely used to study the state of water in solids.[10−14] This technique allows to delineate quantitatively the different types of water in the hydrogel matrix: the amounts of freezable (normal or near-normal) and nonfreezable (bound) water are determined.

On the other hand, polymers which have high potentials as useful materials in biomedical and biotechnological fields are required to be biocompatible. The biocompatibility of the polymers is mainly dependent on the physicochemical and biological interactions between the polymer surface and biomolecules. Contact angle goniometry with test liquids is a suitable method for the characterization of solid surfaces. It is one of the most surface sensitive methods since for nonporous systems only the uppermost atomic layers take part in the interaction with the liquid being responsible for the formation of a certain contact angle. This technique has been successfully applied in biocompatibility studies, and some relationships between the surface energy and cell adhesion,[15] fibroblasts spreading[16,17] or interaction of blood proteins[18,19] to polymeric surfaces have been established.

In previous papers we have modified the characteristics of the poly(2-hydroxyethyl methacrylate) by means of the introduction of a hydrophobic monomer such as furfuryl acrylate[9] or a cross-linking agent such as triethylene glycol dimethacrylate.[20] In this paper we have considered the incorporation of a highly hydrophobic acrylate, 2-ethylhexyl acrylate. This hydrophobic monomer not only will modify the swelling behavior but also, due to its plasticizing character, will impart film-forming characteristics to copolymeric films, giving soft and tacky surfaces.

This paper reports on the synthesis of polyacrylic hydrogels by copolymerization of 2-hydroxyethyl methacrylate, H, with 2-ethylhexyl acrylate, E, at different feed compositions. First, copolymerization reactions were carried out in solution at low conversion in order to determine the reactivity ratios and the chemical distribution of the comonomeric units along the macromolecular chains. Second, copolymeric films were

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prepared by bulk copolymerization for swelling experiments. The dynamic swelling process and diffusional behavior as well as the organization of water inside the gel were analyzed. Also, the surface free energy of the copolymers was determined by contact angle measurements.

Materials

2-Hydroxyethyl methacrylate, H, (Fluka) and 2-ethylhexyl acrylate, E, (Fluka) were distilled under nitrogen reduced pressure before use. H used for kinetic determinations was previously purified[21] to distillation in order to remove ethylene glycol dimethacrylate and methacrylic acid impurities. The solvent, *N*,*N*-dimethylformamide (Scharlau), and methylene iodine (Merck), were used without further purification. The initiator, 2,2′-azobisisobitironitrile, AIBN, (Merck) was purified by fractional crystallization from methanol, mp 104 °C.

Experimental Section

Copolymerization Reaction. The copolymerization reaction of H and E was carried out in solution of *N*,*N*-dimethyl formamide, DMF, (1 mol L^{-1}) at 50 °C using AIBN as the initiator. The monomer solution with feed compositions between E/H = 20/80 and 80/20 was previously degassed for 15 min. The reaction time was adjusted to reach an overall copolymer conversion less than 5 wt %. Copolymers rich in E were purified with 2-propanol/hexane and copolymers rich in H were purified with chloroform/diethyl ether. All of them were washed and dried until constant weight.

Preparation of Films. Films of H/E were obtained by radical bulk copolymerization carried out in cylindrical Teflon molds (30 mm diameter and 5 mm deep). The monomer mixture consisted of H and E in ratios ranging from H/E = 95/5 to 60/40 wt %, and AIBN (1 wt %) as the initiator. The comonomer mixture was degassed with nitrogen for 15 min and then poured into the Teflon mold. To facilitate complete polymerization, the reaction was allowed to proceed for 48 h at 60 °C. The copolymer films were easily separated from the Teflon disk mold and soaked with a mixture of 2-propanol/water (80/20 v/v) at room temperature for 24 h. After this period the liquid mixture was renovated and vessel containing the membrane was sonicated during 60 min. The film was exhaustively dried at reduced pressure until a constant weight was attained. The actual composition of the films was determined by the analysis of the corresponding ^{1}H-NMR spectra. In all the cases the composition of the copolymer films prepared at total conversion was similar to that of the monomer feed, considering a deviation of ±2 wt % associated with the accuracy of the ^{1}H-NMR spectroscopy. Finally the dry film with a thickness of 200 ± 10 μm, was cut into fragments of about 1 to 1.5 cm^2 and kept under vacuum up to the swelling experiments.

Swelling Behavior. Copolymer films weighed accurately were immersed in distilled water at the temperature of interest (25, 38, or 50 °C) and left until equilibrium was attained. Water uptake (W = weight of water in the gel/weight of dry gel) was determined by gravimetry. The swelling behavior was followed by measuring the weight gain with the time of immersion after drying the surface. Measurements were taken every 15 min until equilibrium was attained, which was considered to be accomplished when three consecutive measurements gave the same weight. The equilibrium was reached after an immersion time between 4 and 12 h, depending on the composition of the film and the temperature of the experiment.

Quantitative Analysis of Chemical Compositions. Copolymer composition was determined by means of ^{1}H-NMR spectroscopy with a Varian XL300 spectrometer using chloroform-*d* or DMSO-*d* as solvents, depending on the composition, and tetramethylsilane as internal reference.

Surface Characterization. The contact angle measurements were performed with a Contact Angle Measuring System G10. The surface free energy was calculated by using the equations proposed by Owens[22]

$$(1 + \cos\theta)\gamma_l/2 = (\gamma_s^{\,d}\,\gamma_l^{\,d})^{1/2} + (\gamma_s^{\,p}\,\gamma_l^{\,p})^{1/2} \quad (1)$$

$$\gamma_s = \gamma_s^{\,d} + \gamma_s^{\,p} \quad (2)$$

where γ_s and γ_l are the surface free energies of the solid and liquid and γ_s^d, γ_s^p, γ_l^d and γ_l^p are the dispersion force components and polar force components of the surface free energy of the solid and the liquid, respectively. The liquids used for this purpose were methylene iodide and distilled water. The dispersion force component and the polar force component of the surface energy of water are 21 and 51 mN m^{-1} respectively, and the dispersion force component of the methylene iodine is 50 mN m^{-1}.

Amount of Water from Differential Scanning Calorimetry, DSC. DSC analysis was performed with a Perkin-Elmer, DSC-4 calorimeter interfaced to a thermal analysis data system. The swollen film (10−20 mg) was placed in the aluminum pan, cooled with liquid nitrogen to −60 °C and then heated at 5 °C/min to +50 °C. Films with different hydration degrees were prepared by room temperature evaporation of water from films previously swollen up to equilibrium. After the appropriate weight of the sample was reached, the film was covered with a Teflon envelope in order to equilibrate the system and to guarantee the homogeneous distribution of water in the film.

Table 1. Copolymer Composition and Conditional Probabilities for the Radical Copolymerization of 2-Ethylhexyl Acrylate, E, with 2-Hydroxyethyl Methacrylate, H, in DMF Solution, Using AIBN as Initiator at 50 °C[a]

F(E), feed	f(E), copolymer	P_{EH}	P_{HE}
0.20	0.085	0.93	0.09
0.40	0.21	0.84	0.21
0.50	0.27	0.77	0.28
0.60	0.36	0.70	0.37
0.80	0.57	0.46	0.61

[a] F(E): mole fraction of E in the feed. f(E): mole fraction of E in the copolymer.

Results and Discussion

Kinetic Treatment and Statistical Copolymerization Data. Copolymerization experiments at various initial comonomer feed compositions were carried out in solution and at low conversion (<5 wt %) in order to estimate the reactivity ratios. The copolymer composition was obtained by ^{1}H-NMR spectroscopy. The integrated intensity of the signals assigned to $-OCH_2-$ (3.55 δ) groups; $-CH_2-$, $-CH-$ (1.25 δ), and $-CH_3$ (0.85 δ) protons of the alkyl groups corresponding to the E unit were compared with those of $-OCH_2-$ (3.9 δ) protons and $-(CH_3)_\alpha$ (0.85 δ) protons pertaining to the H unit.[9] Results are collected in Table 1. The compositions of the copolymers are quite different from those of the comonomer feed, the former being richer in 2-hydroxyethyl methacrylate than the latter.

The reactivity ratios were determined by using both linearization methods (Fineman-Ross, FR,[23] and Kelen-Tudos, KT[24]) and the nonlinear least-squares analysis by Tidwell and Mortimer, TM.[25] Figure 1 shows the elliptical diagram of the 95% confidence limit of the reactivity ratios in E/H copolymerization determined according to the mathematical treatment by Tidwell and Mortimer. This method provides also the optimum values which are $r_E = 0.29$ and $r_H = 2.54$, implying that the propagating species ending in 2-ethylhexyl acrylate are much more reactive towards 2-hydroxyethyl methacrylate molecules than towards its own monomer. The

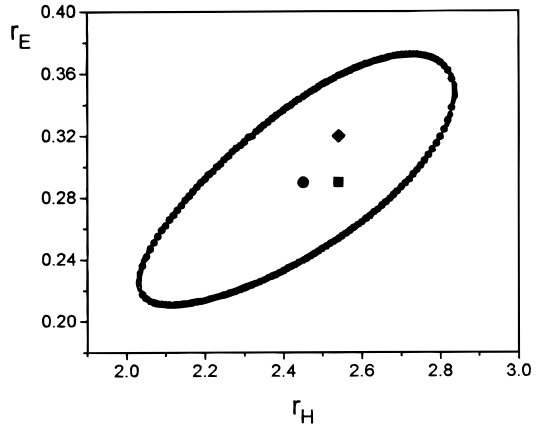

Figure 1. 95% Confidence diagram for the reactivity ratios of E and H determined by the nonlinear least-squares method suggested by Tidwell and Mortimer. Values of reactivity ratios: (■) Tidwell-Mortimer; (◆) Kelen-Tudos; (●) Fineman-Ross.

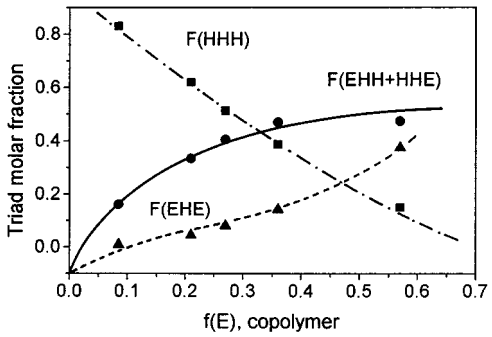

Figure 2. Content of H centered triads as a function of the copolymer composition for the copolymerization of 2-ethylhexyl acrylate with 2-hydroxyethyl methacrylate.

Table 2. Reactivity Ratios of the Free Radical Copolymerization of the E/H Pair in *N,N*-Dimethylformamide at 50 °C Using AIBN as Initiator (FR = Fineman−Ross; KT = Kelen−Tudos; TM = Tidwell and Mortimer)

method	r_E	r_H	$1/r_E$	$1/r_H$	$r_E \times r_H$
FR	0.29 ± 0.017	2.45 ± 0.098	3.45	0.4	0.71
KT	0.32 ± 0.106	2.54 ± 0.105	3.12	0.39	0.81
TM	0.29	2.54	3.45	0.39	0.79

propagating radicals ending in the 2-hydroxyethyl methacrylate unit, on the other hand, will be much more reactive towards its own monomer, which will give rise to the formation of long sequences of hydroxyethyl methacrylate in the copolymeric chains. All values of reactivity ratios are summarized in Table 2. The values obtained by using the linearization methods are close to those estimated by the nonlinear least-squares method at the moderate conversions studied in the present work.

The conditional probabilities P_{ij} (i,j = E, H) defined as the probability for the addition of monomer units j to free radical i ends were calculated statistically from the optimum values of reactivity ratios and are collected in Table 1. The statistical diagrams of H-centered sequences in terms of triads were determined according to the classical Mayo−Lewis model.[26] Figure 2 shows the variation of the mole fraction of H centered triads with copolymer composition. The mole fraction of homotriads decreased and that of alternating triads increased with the E content in the copolymer. The mole fraction of heterotriads also increased with the content of E in a wide interval of copolymer composition, from $f(E) = 0.09$ to $f(E) = 0.60$. This shows that the probability of finding consecutive H units along the macromolecules is noticeable, even for copolymer compositions rich in 2-ethylhexyl acrylate. From a morphological point of view, it is interesting to stress that the films prepared with an E content higher than 10 mol-% are not transparent in the dry state and the whitening intensity increases as the fraction of E in the copolymer samples increased. According to the diagrams drawn in Figure 2, it is reasonable to consider that the sequences of EHE, EHH, and HHE triads probably are not compatible with the HHH sequences giving rise to the segregation of microdomains rich in E units. This morphology would explain the whitening of the films prepared. However, it was not possible to detect the presence of such microdomains by DSC because very wide glass transitions were observed due to the relatively high hygroscopic character of the dry films. After hydration the films became transparent which indicates that although the hydrophobic microdomains could be formed, their size is relatively small.

Table 3. Values of the Equilibrium Water Content W_∞, and Diffusion Coefficient, D, for the H/E Copolymers at 25, 38, and 50 °C

E content in the film (wt %)	W_∞ (g H_2O/g of polymer)			$D \times 10^7$ (cm^2/s)		
	25 °C	38 °C	50 °C	25 °C	38 °C	50 °C
(poly-H)	0.56	0.53	0.52	1.86	2.16	2.44
5	0.45	0.43	0.4	0.89	1.09	1.59
10	0.40	0.38	0.36	0.75	0.84	1.44
15	0.36	0.34	0.33	0.68	0.78	1.36
20	0.28	0.31	0.29	0.68	0.76	1.32
30	0.21	0.24	0.24	0.67	0.76	1.27
40	0.15	0.17	0.18	0.67	0.76	1.25

Swelling Behavior. H/E copolymer films with amounts of E in the interval 5−40 wt % were used for swelling experiments. The typical stiff and transparent poly(2-hydroxyethyl methacrylate), poly-H, film was strongly modified by the presence of the hydrophobic E units. Films become more opaque, soft, and flexible with the E content as a consequence of the effect of the 2-ethylhexyl side groups on the E units. This was stated by a clear shift to lower temperatures of the apparent glass transition of the copolymer systems measured by DSC, in addition to a widening of the transition interval, which in some cases reached more than 50−60 °C. After immersion in water the films readily swelled up to an extension depending on the chemical composition and the temperature of the experiment. Values of the equilibrium water content, W_∞, are summarized in Table 3. Figure 3 shows the kinetic behavior of films at 50 °C. Diagrams with the same trend were obtained at 25 and 38 °C. It is clear that the absorption of water depends noticeably on the composition of the copolymer films, but in any case, the equilibrium hydration degree was reached in a period of time between 4 and 12 h, depending on the composition of the film and the temperature of the experiment.

The dependence of W_∞ on composition is plotted in Figure 4. The effect of the introduction of some long hydrophobic side groups in the hydrophilic film provided an abrupt drop in W_∞, e.g., copolymer films with 5 wt % of E. Afterward, an almost linear decrease of equilibrium water uptake—with intensity depending on the temperature of the experiment—was obtained as the films become richer in the E monomer. A similar behavior has been reported in the literature for the 2-hydroxyethyl methacrylate/furfuryl acrylate[9] and vinyl pyrrolidone/furfuryl methacrylate[27] systems. The

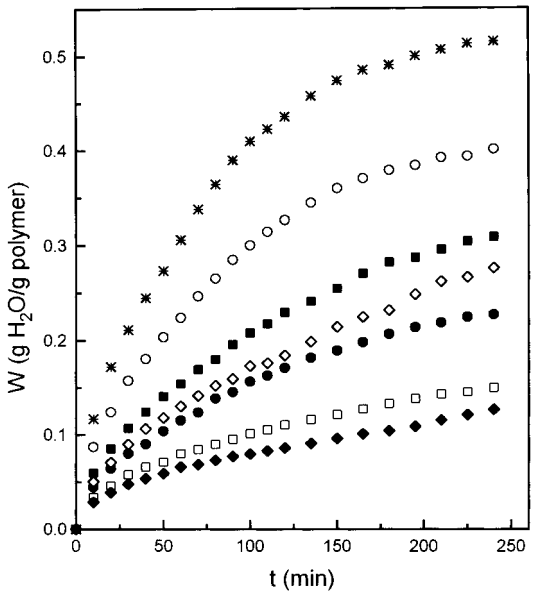

Figure 3. Sorption isotherms for H/E copolymers with different composition at 50 °C. (*) poly-H; (○) 5, (■) 10, (◇) 15, (●) 20, (□) 30, and (◆) 40 wt % of E in the copolymers.

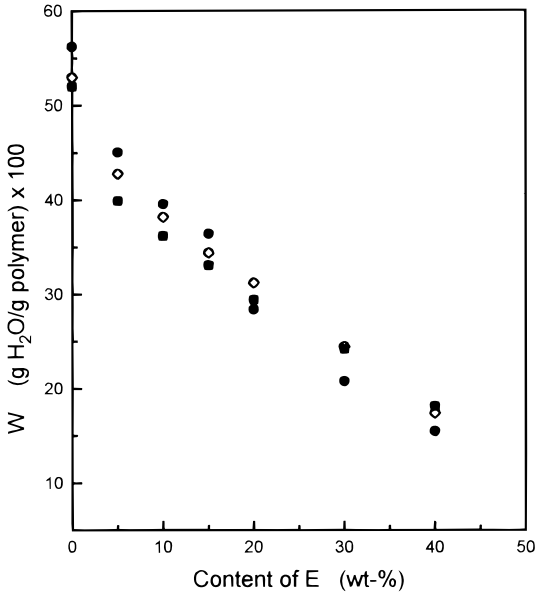

Figure 4. Equilibrium water content, W_∞, of H/E hydrogels as a function of the content of E at different temperatures: (●) 25, (◇) 38, and (■) 50 °C.

data drawn in Figure 4 seem to indicate that the variation of the swelling behavior is strongly dependent on the average composition although the effect of the temperature is less noticeable. In fact, all the systems studied in this work were very flexible at any hydration degree, and therefore, the influence of temperature in the interval studied has to be smaller than that of the composition. However, a deeper analysis of the hydration data vs the experimental temperature provides interesting results and conclusions. In this way, the temperature dependence of W_∞ was analyzed by the application of the Gibbs−Helmholtz equation[11]

$$\mathrm{d}(\ln(W_\infty))/\mathrm{d}(1/T) = -\Delta H_\mathrm{m}/R \qquad (3)$$

where R is the gas constant and ΔH_m is the enthalpy of mixing between the dry polymer and an infinite amount of water. When plotting W_∞ against the reciprocal of the swelling temperature (Figure 5) straight lines with

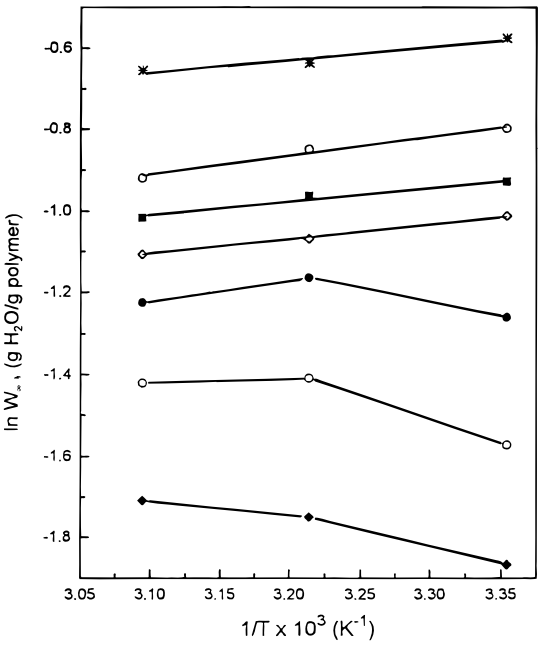

Figure 5. Temperature dependence of the equilibrium water content, W_∞, for H/E copolymers: (*) poly-H; (○) 5, (■) 10, (◇) 15, (●) 20, (□) 30, and (◆) 40 wt % of E in the copolymers.

positive slopes were obtained for poly-H and for the copolymer films with less than 20 wt % of E, which means an exothermic mixing process. The slope of these lines is independent on the composition within the experimental error, giving and average value of $\Delta H_\mathrm{m} = -3.0$ kJ/mol. However, the copolymers with an E content higher than 20 wt % gave rise to a change on the temperature of swelling dependence, and a positive ΔH_m was obtained for the sample with an E content of 40 wt %. The change in the sign of ΔH_m with composition has also been reported for inhomogeneous poly(acrylonitrile−acrylamide−acrylic acid) gels,[11] and the existence of a copolymer composition with temperature independent swelling has been postulated. On the light of the above results, this so-called "ideal gel", characterized by $\Delta H_\mathrm{m} = 0$, might be obtained for a H/E copolymer with a composition lying somewhere in between 15 and 20 wt % of E.

Kinetic Analysis of the Water Sorption Process. Films of H/E copolymers ranging from H/E = 95/5 to 60/40 molar ratios showed Fickian behavior according to the approximation of Fick's law[28] (eq 4), which can be applied to thin flat sheets in which diffusion through the edges may be neglected.

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

M_t and M_∞ represent the water uptake at time t and at infinite time, respectively, D is the diffusion coefficient, and l is the average thickness of the film. Results are plotted in Figure 6. From the slopes of the straight lines the diffusion coefficients were obtained, values being reported in Table 3. A drastic drop in the diffusion coefficient of the films was observed after the introduction of some E units in the poly-H hydrogel. From then on, a monotonic decrease in the diffusion coefficient of the films with the increase in E content was observed. The diffusion coefficient increased with the swelling temperature for all compositions. An Arrhenius equation (eq 5) was applied to the experimental data, and the results are plotted in Figure 7.

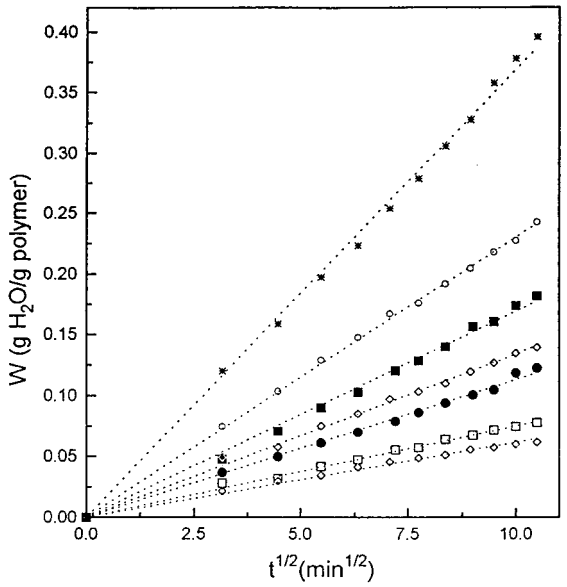

Figure 6. Sorption kinetics according to eq 4 for H/E copolymers with different compositions: (*) poly-H; (○) 5, (■) 10, (◇) 15, (●) 20, (□) 30, and (◇) 40 wt % of E in the copolymers.

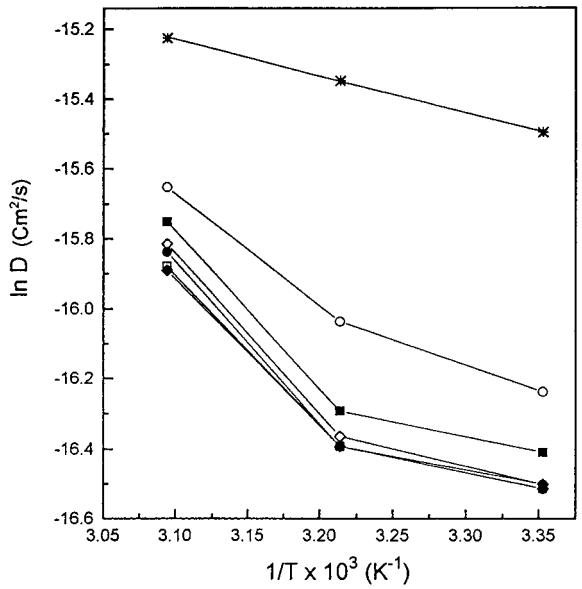

Figure 7. Temperature dependence of the diffusion coefficient, D, for the H/E copolymers with different composition. (*) poly-H; (○) 5, (■) 10, (◇) 15, (●) 20, (□) 30, and (◆) 40 wt % of E in the copolymers.

$$D = D_0 \exp(-E_D/RT) \quad (5)$$

where E_D is the apparent activation energy for the diffusion process. The expected linear dependence of the logarithm of D on $1/T$ was only obtained for poly-H, giving an activation energy of 8.8 kJ/mol, a typical value for diffusion processes. However, the E/H copolymers did not exhibit an Arrhenius behavior over the temperature interval studied, the deviation increasing with the E content in the copolymer films. The reason for this deviation could lie on an inhomogeneity of the samples due to incompatibility between the long hydrophobic alkyl residues and the hydrophilic hydroxyethyl groups. This supports the idea of segregation of the components in microdomains, the H segments being the continuous phase, at least in a wide composition interval ranging form 95 to 50 wt % of H units.

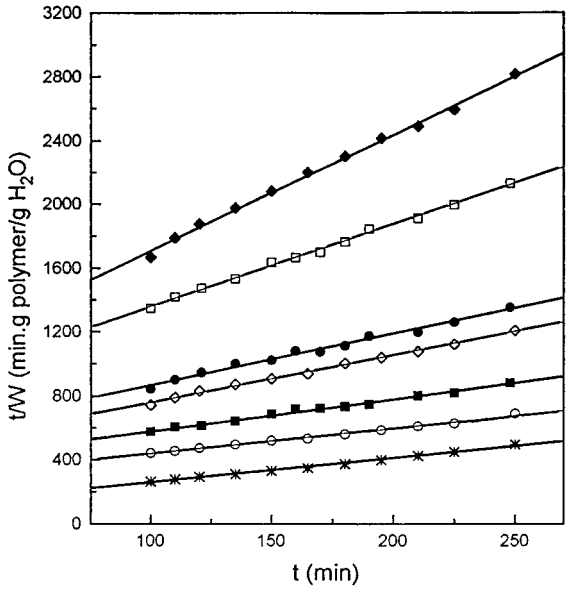

Figure 8. Reciprocal of the average swelling rate, t/W, as a function of the time of treatment for the H/E copolymers. Straight lines correspond to the least squares fit of experimental points to eq 6: (*) poly-H; (○) 5, (■) 10, (◇) 15, (●) 20, (□) 30, and (◆) 40 wt % of E in the copolymers.

On the other hand, second order kinetics proposed by Schott[29] (eq 6) were applied for long swelling periods.

$$t/w = A + Bt \quad (6)$$

where w is the swelling or water uptake at time t, $B = 1/W_\infty$, the inverse of the maximum swelling and $A = 1/(dW/dt)_0$, the reciprocal of the initial swelling rate. The diagrams obtained by the application of the experimental data to eq 6 gave straight lines with excellent correlation coefficients, as it is illustrated in Figure 8 for the swelling experiments at 38 °C. The same pattern was obtained for the data at 25 and 50 °C.

Bound and Nonbound Water in Hydrogels from DSC Experiments. DSC thermograms for copolymeric films containing 5 wt % of the E monomer with various unsaturated water uptakes (26.9−42.9 wt %) are shown in Figure 9. The thermogram corresponding to the sample with hydration degree of 26.9 wt % showed no endothermic peak around the melting point of water, indicating that the water present in the hydrogel at this hydration degree must be directly bound to the copolymer and it should be of the nonfreezing type. However, a slight deviation of the base line was observed around −20 °C, which was assigned to a glasslike transition.[30] The thermograms of copolymer films containing higher water uptakes showed an asymmetric endothermic peak at 0.3−0.7 °C associated with the melting of the pure crystallized water, which indicates that from a hydration degree of 35% a certain amount of water not directly bound to the polymer is present in the hydrogel. The thermogram of the water-equilibrated gel exhibited an exotherm peak around −6 °C which has been associated to devitrification of glassy water or tightly bound water.[13,31,32] Also, in the thermogram of the sample with 35 wt % water content an incipient exothermic peak can be observed.

The content of bound water is the limiting value of the water content in a gel at zero enthalpy of fusion of the gel. This extrapolated value was taken from the plot of the DSC melting enthalpy of the gel vs the nonequilibrated water content in the gel (Figure 10). A

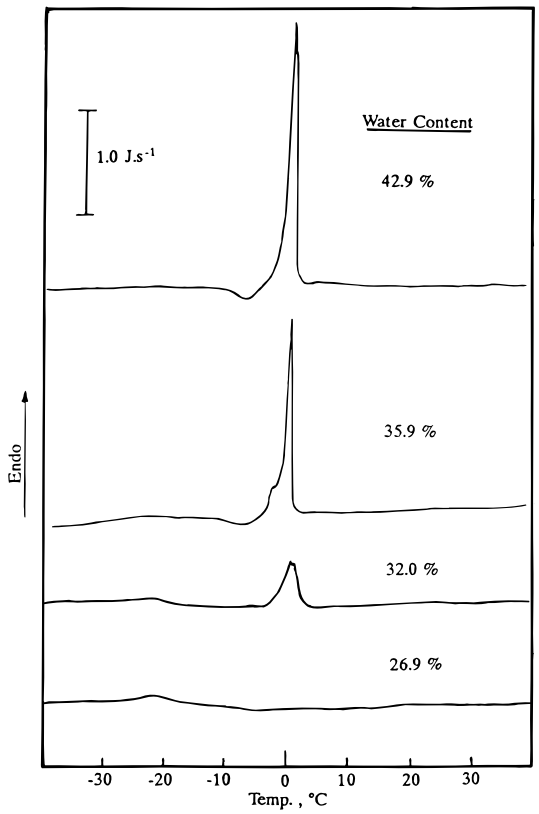

Figure 9. DSC thermograms for the H/E copolymer with 5 wt % of E with different water contents as indicated in the diagram.

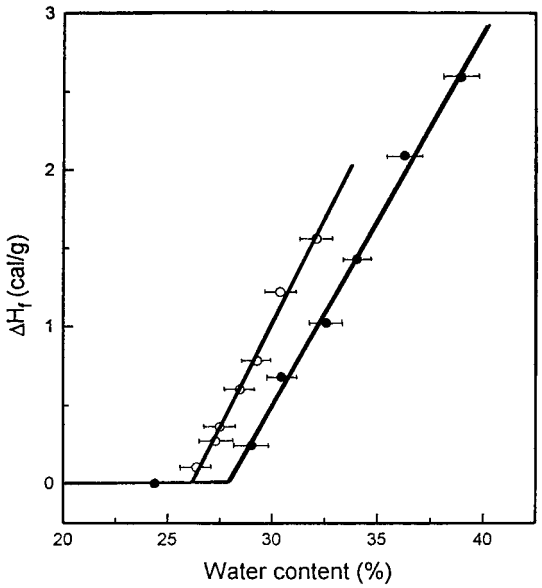

Figure 10. Plot of the melting enthalpy, ΔH_f, as a function of the water content for H/E copolymers with 5 (●) and 10 (○) wt % of E. Both ΔH_f and water content are related to the dry polymer weight.

content of bound water of 28 ± 2 wt % for the copolymer with 5 wt % of E and 26 ± 3 wt % for that with 10 wt % of E were obtained. These values compare well with the value reported for poly-H (13) (25 ± 4 wt %) recorded at the same scanning rate, within experimental error.

Surface Character and Properties. The surface characteristics of H/E copolymer films were studied in a wide interval of copolymer composition, measuring the contact angle by the classical method of sessile drop. Table 4 shows the relationship between the E content

Table 4. Values of Contact Angles (Sessile Drop) of Water and Methylene Iodide on E/H Copolymer Films at Room Temperature, Together with Values of Surface Energy of Solid, SES, with the Dispersive, *d*, and Polar, *p*, Components

E content in the copolymer (wt %)	θ_{water} (deg)	θ_{diiod} (deg)	SES (mN/m)	*d* (mN/m)	*p* (mN/m)
(poly-H)	50	38	58.4	40.3	18.1
12	78	49	40.1	34.6	5.4
27	78	49	40.0	35.0	5.1
34	80	51	39.4	34.8	4.6
44	82	54	36.7	32.4	4.3
65	83	56	35.2	30.7	4.5
(poly-E)	90	63	31.0	28.0	4.4

and the contact angle of water and methylene iodine on the surface of H/E copolymer films, poly-H and poly-E films. The surface energy of solid, SES, was evaluated by using the equations suggested by Owens (eqs 1 and 2), and the values obtained are collected in Table 4. It is necessary to take into consideration that the accuracy of the technique depends on the quality of the optical components of the equipment used in the experimental determination of the contact angle tan θ. In particular, according to the specifications of the equipment used in this work, it can be considered that the errors are around 4−5%. This means that values obtained in a wide interval of compositions of H/E copolymers are rather similar considering the standard deviations, but the most important conclusion is the noticeable effect of the introduction of component E on the character of the surface of the corresponding copolymer samples. Poly-H is a hydrophilic material with a high surface energy containing a strong polar contribution (18 mN/m).[33] Copolymeric films with an E content in the range 12−65 wt % exhibited values of the total surface energy lower than that of poly-H. The reduction of SES was due to the decrease of both dispersive and polar components, which were higher for the polar than for the dispersive components. It seems as if the long alkyl residues were concentrated on microdomains at the surface, in order to minimize the SES or the interfacial free energy of the polymer, in the same way as happens with copolymers of some noncompatible components, in particular, block copolymers or graft copolymers.[34] In addition, the reactivity ratios of this pair of monomers support the formation of long sequences of H units along the copolymeric chains, mainly for copolymer compositions rich in 2-hydroxyethyl methacrylate (see Figure 2). This could explain the steep decrease in the SES even when small amounts of the acrylate are present in the copolymer. Accordingly, Nakamae et al. studying the surface characteristics of EVA copolymers found that surface compositions were different from bulk compositions and that one component was concentrated at the membrane surface.[34] The surface energy values are also consistent with the drop in the diffusion coefficient for polymeric films containing only 2-ethylhexyl acrylate and, also, with the failure of the linear dependence of the logarithm of *D* on 1/*T* for the copolymeric hydrogels.

Conclusions

Highly flexible hydrogels can be prepared by free radical polymerization of 2-hydroxyethyl methacrylate with small quantities of 2-ethylhexyl acrylate (5−30 wt %). The reactivity ratios support the trend to form HH sequences in a wide interval of feed compositions.

Specific interactions of nonfreezable water molecules with the hydrophilic H units and the relatively nonpolar

E units were demonstrated by DSC. The presence of small amounts of the hydrophobic monomer did not seem to influence the nonfreezing water content with respect to that observed for poly-H, although the freezing water content was reduced.

Surface characterization of the copolymer films revealed a considerable decrease of the surface energy of the solid when introducing 10 wt % of the E monomer, the reduction being observed mainly in the polar contribution.

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References and Notes

(1) Franklin, V. J.; Bright, A. M.; Tighe, B. J.; *Trends Polym. Sci.* **1993**, 1, 9−16.
(2) Peppas, N. A.; Korsmeyer, R. W. In *Hydrogels, Medicine and Pharmacy;* Peppas, N. A., Ed.; CRC Press: Boca Raton, FL, 1987; Vol III, pp 109−135.
(3) Ratner, B. D. *J. Biomed. Mater. Res.* **1993**, *27*, 283−287.
(4) Kin, S. W.; Feijen, J. *CRC Crit. Rev. Biocompatibility* **1985**, *1*, 229−260.
(5) Lee, P. I. In *Treatise on controlled drug delivery. Fundamentals. Optimization. Applications*; Kydonieus, A., Ed.; Marcel Dekker, Inc.: New York, 1992, pp 155−195.
(6) Kim, S. W.; Petersen, R. V.; Feijen, J. In *Drug. Design;* Ariens, J., Ed.; Academic Press: New York, 1980; Vol X, pp 193−250.
(7) Williams, D. F.; *Concise encyclopaedia of medical and dental materials*, Pergamon Press: Oxford, England, 1990.
(8) Chirila, T. V.; Chen, Y. Ch.; Griffin, B. J.; Constable, I. J. *Polym. Int.* **1993**, *32*, 221−232.
(9) Peniche, C.; Zaldívar, D.; Gallardo, A.; San Román, J. *J. Appl. Polym. Sci.* **1994**, *54*, 959−968.
(10) Allen, P. E. M.; Bennett, D. J.; Williams, D. R. G. *Eur. Polym. J.* **1993**, *29*, 231−236.
(11) Shiaw-Guang, Hu. D.; and Lin, M. T. S.; *Polymer* **1994**, *35*, 4416−4422.
(12) Andrade, J. D.; in *Surface and interfacial aspects of biomedical polymers*; Andrade, J. D., Ed.; Plenum Press: New York, 1985; Vol. 1, Chapter 2, p 214.
(13) Smyth, G.; Quinn, F. X.; Mc Brierty, V. J. *Macromolecules* **1988**, *21*, 3198−3216.
(14) Pedley, D. G.; Tighe, B. *Br. Polym. J.* **1979**, *11*, 130−136.
(15) Baier, R. E.; Meyer, A. E.; Natiella, J. R.; Natiella, R. R.; Carter, J. M. *J. Biomed. Mater. Res.* **1984**, *18*, 337−355.
(16) Schakenraad, J. M.; Busscher, H. J.; Wilderuur, C. R. H.; Arends, J. *J. Biomed. Mater. Res.* **1986**, *20*, 773−784.
(17) Van der Valk, P.; Van Pelt, A. W. J.; Busscher, H. J.; de Jong, H. P.; Wilderuur, H.; Arends, J. *J. Biomed. Mater. Res.* **1983**, *17*, 807−817.
(18) Uyen, H. M. W.; Schakenraad, J. M.; Sjollema, J.; Noordmans, J.; Jongebloed, W. L.; Stokroos, I.; Busscher, H. J. *J. Biomed. Mater. Res.* **1990**, *24*, 1599−1614.
(19) Lu, D. R.; Park, K. *J. Colloid Interface Sci.* **1991**, *144*, 271−281.
(20) Peniche, C.; Cohen, M. E.; Vázquez, B.; San Roman, J. *Polymer* **1977**, *38*, 5977−5982.
(21) Fort, R. J.; Polyzoidis, T. M. *Eur. Polym. J.* **1976**, *12*, 685−689.
(22) Owens, D. K. *J. Appl. Polym. Sci.* **1969**, *13*, 1744−1747.
(23) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259−265.
(24) Kelen, T.; Tudos, F. *J. Macromol. Sci.* **1975**, *A9*, 1−27.
(25) Tidwell, P. W.; Mortimer, G. G. A. *J. Polym. Sci.* **1965**, *A3*, 369−387.
(26) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594−1601.
(27) Zaldivar, D.; Peniche, C.; Gallardo, A.; San Roman, J. *Biomaterials* **1993**, *14*, 1073−1079.
(28) Crank, J. *The Mathematics of Diffusion*, Clarendon: Oxford, England, 1978; p 239.
(29) Schott, H. J. *Macromol. Sci.-Phys.* **1992**, *B31*, 1−9.
(30) Rault, J.; Gref, R.; Ping, Z. H.; Nguyen, Q. T.; Neel, J. *Polymer* **1995**, *36*, 1655−1661.
(31) Quinn, F. X.; Mc Brierty, V. I.; Wilson, A. C.; Friends, G. D. *Macromolecules* **1990**, *23*, 4576−4581.
(32) Mc Brierty, V. J.; Quinn, F. X.; Keely, C.; Wilson, A. C.; and Friends, G. D. *Macromolecules* **1992**, *25*, 4281−4284.
(33) Okumura, M.; Kinomura, K. *Makromol. Chem. Phys.* **1994**, *195*, 1953−1963.
(34) Nakamae, K.; Miyata, T.; Matsumoto, J. *J. Membr. Sci.* **1992**, *69*, 121−127.
(35) Nakamae, K.; Miyata, T.; Matsumoto, J. *J. Membr. Sci.* **1992**, *75*, 163−169.

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