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ACRYLIC ACID/METHYL METHACRYLATE HYDROGELS. I. EFFECT OF COMPOSITION ON MECHANICAL AND THERMODYNAMIC PROPERTIES

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Key Words: Hydrogel, Mechanical Properties, Swelling, Freezing Water, Hydrophylic, Hydrophobic, Thermodynamic Properties

ABSTRACT

The mechanical and thermodynamic properties of poly(acrylic acid-co-methyl methacrylate) hydrogels with varying ratios of AA/MMA are reported. Swelling capacity increases but elasticity decreases as the content of AA in the hydrogels increases. Thermodynamic analysis indicates that swelling is an unfavor-

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able ($\Delta\overline{G}_1 > 0$) and endothermic ($\Delta\overline{H}_1 > 0$) process. Both thermodynamic quantities increase with increasing hydrophobic nature of the hydrogel. The amount of freezing and non-freezing water in the hydrogels was determined by DSC. The ratio of non freezing to total water content increases with the increasing hydrophobic nature of the hydrogels.

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INTRODUCTION

A gel is a polymeric network that retains a large amount of a solvent and swells without dissolving. A hydrogel is then a gel that expands substantially in contact with water. Currently, hydrogels are encountered in drug and water-and-nutrients delivery systems, superabsorbent sanitary towels and diapers, prothesis, soft lenses, etc. [1-7]. In all these applications, the swelling capacity and the mechanical properties, particularly in the swollen state, play important roles [1, 8].

Usually, hydrogels in a highly swollen state have poor mechanical properties. One way to simultaneously modify the mechanical properties and the swelling capacity, and then, to synthesize custom-made hydrogels, is to copolymerize hydrophilic and hydrophobic monomers in varying ratios. In general, the presence of a hydrophilic monomer in the hydrogel increases its swelling capacity while the presence of a hydrophobic monomer improves significantly the mechanical properties [9].

In this work, we investigate the influence of composition on the swelling capacity as well as on the mechanical and thermodynamic properties of hydrogels of acrylic acid (AA) and methyl methacrylate (MMA) of varying ratios of AA/MMA. Moreover, we examine the structure of water in these hydrogels by differential scanning calorimetry.

EXPERIMENTAL

Materials

Acrylic acid (AA), 99% pure from Fluka, was passed through a silica gel column to remove the inhibitor (methyl ether hydroquinone). Methyl methacrylate (MMA) from Polyscience was used as received. N, N'-methyl-enbisacrylamide (NMBA) with a purity of 98% (Fluka) was further purified by recrystallization from methanol. 2,2’-Azobis(amidinopropane) or V-50 was 99.5% pure from Wako. It was further purified by recrystallization from methanol. Ethanol was 96% (v/v) from Panreac. Doubly distilled deionized water, drawn from a Millipore Milli-Q water purification system, was used for swelling and DMA tests.

Synthesis

Five hydrogels with different compositions were synthesized by varying the weight ratio of AA to MMA from 100/0 to 60/40. To identify the composition of the hydrogels we used the notation AAxx where xx indicates the weight content of acrylic acid. With the exception of AA100, the hydrogels were prepared with 0.1 g V-50/100 mL of total monomers. With AA100, the concentration of V-50 was 0.075 g/100 mL of monomer due to the high reactivity of this monomer. The concentration of the crosslinking agent, NMBA, was 0.1 g/100 mL of monomers in all cases. For the synthesis, the appropriate amount of V-50 was dissolved in 1 mL of water in a test tube; NMBA was dissolved in 6 mL of ethanol in another test tube, and then, 4 mL of total monomers were added. The contents of both tubes were purged with nitrogen for 10 minutes and then mixed and heated to 50°C for 6 hours. The products, in the shape of cylinders, were immersed in ethanol and then in water for several days to remove non reacted monomers and other soluble materials. Both solvents were changed several times to optimize the extraction process. Then the cylinders were cut in the shape of disks and dried in an oven at 40°C until constant weight. The dry disks were sanded with a mild sandpaper until their thickness was ca. 1 mm. The dimensions of the discs were measured with a micrometer. Then, they were weighed (m_o) and immersed in deionized water until the equilibrium swelling was achieved at 25, 30, 37 or 45°C. The water content at equilibrium or equilibrium swelling, W_{eq}, was calculated with:

$$W_{eq}(\%) = \frac{(m_f - m_o)}{m_o} \text{x} 100 \qquad (1)$$

where m_f and m_o represent the weights of the swollen sample at equilibrium swelling and of the xerogel, respectively.

The volume fraction of polymer within a hydrogel, Φ^2, at a particular temperature is:

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$$\phi_2 = \left(\frac{D_o}{D}\right)^3 \qquad (2)$$

where D_o and D are the diameters of dry and equilibrium swollen discs, respectively.

Compression Measurements

A Perkin-Elmer DMA7 Dynamic Mechanical Analyzer with a parallel plate geometry was used for compression stress-strain tests. The hydrogel discs were immersed in deionized water during measurements to minimize water losses. The elastic moduli, G, of the hydrogels were determined in the compression mode at low deformations at which the stress, τ, depends linearly on the deformation (λ-1) - where τ is the ratio of the deformed to the initial length, as follows [10]:

$$\tau = G(\lambda - \lambda^{-2}) \qquad (3)$$

The effective crosslinking density, ν_e, was estimated from G according to [11]:

$$G = RT\nu_e\phi^{-1/3;2} \qquad (4)$$

where R is the ideal gas constant and T the absolute temperature.

Differential Scanning Calorimetry

Thermograms of swollen hydrogels were obtained with a Mettler TA4000 Differential Scanning Calorimeter equipped with a refrigeration unit. Excess water was removed by tapping the surface of the hydrogels with paper filter. Samples (7 to 12 mg) were then loaded in aluminium cells, which then were sealed. Samples were cooled to -50°C to guarantee that all the water in the sample is frozen. Thermograms were obtained at heating rates of 1 and 5°C/min. The weight of freezing (“free”) water was calculated from the mea-

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sured enthalpy of the water peak, obtained from the area of the melting transition, and the literature value (321.17 J/g) [12]. The amount of non freezing (“bound”) water in the hydrogels was estimated by difference with the total water content. The weight ratio of free water and bound water to the total weight of equilibrium swollen hydrogel are denoted as W_f and W_{nf}, respectively.

RESULTS AND DISCUSSION

Table 1 summarizes the equilibrium swelling properties of the AA/MMA hydrogels measured at 37°C. The equilibrium swelling diminishes as the concentration of MMA in the hydrogels increases because of the higher hydrophobicity of MMA. The decrease is substantial since W_{eq} for the AA100 hydrogel is 86.7% compared to only 48.0% for the AA60 sample. As expected from the swelling behavior, Φ_2 increases as the content of AA in the hydrogels increases (Table 1). Equilibrium swelling also increases with increasing temperature (Figure 1) for all samples. As expected, the equilibrium swelling rises faster with temperature as the hydrogels becomes more hydrophilic, i.e., as composition shifts from AA60 to AA100 (Figure 1).

Elastic moduli of AA/MMA hydrogels were obtained according to Equation 3 from the slope of plots of stress versus strain at small strains where the plots are linear. The Young’s moduli (E) can then be estimated from the values of G since the ratio E/G ranges from 3.0 to 3.2 [13]. Network parameters for the five hydrogels at 37°C are presented in Table 2.

Both E and G increase as the content of MMA in the hydrogels increases and the equilibrium swelling decreases (Tables 1 and 2). Inasmuch as MMA is a more hydrophobic monomer than AA, the increase in content of MMA dimin-

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TABLE 1. Equilibrium Swelling, W_f, and Volume Fraction of Polymer, Φ_2, Measured at 37°C, for the AA/MMA Hydrogels

SAMPLE	W_f (%)	Φ_2
AA100	86.7	0.113
AA90	85.8	0.117
AA80	71.7	0.251
AA70	55.3	0.444
AA60	48.0	0.517

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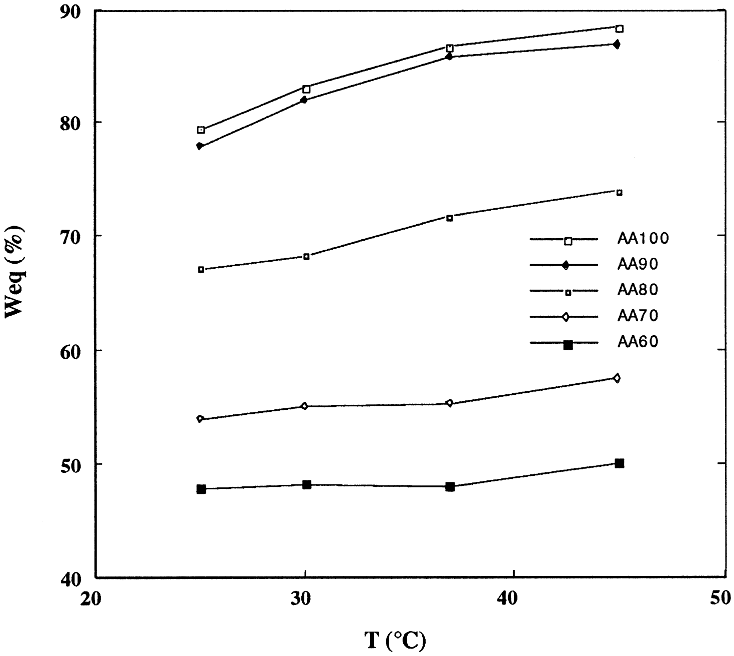

Figure 1. Equilibrium swelling of AA/MMA hydrogels as a function of temperature.

ishes the amount of water, which acts as a plasticizer for the copolymer [14-16] and leads to a more rigid material and, hence, to a larger Young's modulus. The effective crosslinking density, ν_e, estimated with Equation 4, increases rapidly with the concentration of MMA (Table 2), in spite that the type and concentration of crosslinking agent are the same in all cases, which presumably should result in the same crosslinking density in all the hydrogels, ν_t (= cf/2) - where c and f are the concentration and functionality of the crosslinking agent, respectively. Nevertheless, the values of ν_e and of ν_t rarely coincide, even for homopolymer hydrogels [17]. The increase in ν_e with increasing MMA content implies a tighter network which is consistent with the smaller swelling and larger moduli of the hydrogels (Table 1).

From ν_e, the molar mass per crosslink, M_c, can be estimated as:

$$M_c = \rho / \upsilon_e \tag{5}$$

where ρ , the density of the xerogel, was estimated by measuring with a micrometer the dimensions of the dry disks and by weighing them. Table 2 shows that M_c decreases as the concentration of MMA in the hydrogel increases as expected from its inverse proportionality to υ_e.

Table 2 also reports the values of the polymer-solvent interaction parameter, χ, which was calculated with the following expression, which is valid at swelling equilibrium [10]:

$$\ln(1-\phi_2)+\phi_2+\chi\phi_2{}^2+\upsilon_e V_1(\phi_2{}^{1/3}-2\phi_2 f^{-1})=0 \qquad (6)$$

here f = 4 for NBMA and V_1 is the molar volume of water (in dm^3/mol) obtained as [18]:

$$V_1=18.05\times10^{-3}+3.6\times10^{-6}(T-298) \qquad (7)$$

where T is in K. The parameter χ represents the specific interactions among solvent and polymer molecules. χ increases with increasing MMA content (Table 2) as a result of the decreasing molecular interactions between water and the increasingly hydrophobic hydrogel copolymers.

The values of the interaction parameters at four different temperatures for the AA/MMA hydrogels are presented in Table 3. For the five hydrogels studied, χ decreases linearly with temperature with similar slopes, except for the AA100, which exhibits a steeper slope indicating a stronger dependence of χ on temperature due to the more pronounced thermoswelling behavior of the more

TABLE 2. Network Parameters, Measured at 37°C, for the AA/MMA Hydrogels.

SAMPLE	E MPa	G MPa	$\nu_e \times 10^3$ mol/dm^3	χ	M_c kg/mol
AA100	0.13	0.042	7.88	0.54	163.1
AA90	0.14	0.047	8.92	0.54	135.0
AA80	0.30	0.098	23.99	0.60	48.6
AA70	0.46	0.15	45.58	0.72	28.0
AA60	0.54	0.18	56.05	0.79	22.6

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hydrophilic AA100 hydrogel. From the dependence of χ with temperature, the entropic, χ_S, and enthalpic, χ_H, contributions can be obtained from [19]:

$$\chi = \chi_H + \chi_S \tag{8}$$

where

$$\chi_H = -T\left(\frac{d\chi}{dT}\right) \tag{9}$$

and

$$\chi_s = \chi + T\left(\frac{d\chi}{dT}\right) \tag{10}$$

The dependencies of χ, χ_S and χ_H with temperature for the AA70 hydrogel are depicted in Figure 2. Both and are positive and $\chi_S > \chi_H$. This behavior is similar for the other hydrogels. For a given composition, decreases with increasing temperature whereas shows the opposite behavior. At a given temperature, χ_H decreases with increasing MMA content up to AA70 and then it decreases slightly with the AA60 hydrogel [20]. χ_S, on the other hand, always increases with MMA content. To understand this behavior, it is necessary to calculate the partial molar enthalpies, $\Delta\overline{H}_1$, and entropies, $\Delta\overline{S}_1$, of dissolution from the values of χ_H and χ_S as follows:

$$\Delta\overline{H}_1 = RT\phi_2{}^2\chi_H \tag{11}$$

TABLE 3. Interaction Parameter for the AA/MMA Hydrogels as a Function of Temperature.

T (°C)	χ_{AA100}	χ_{AA90}	χ_{AA80}	χ_{AA70}	χ_{AA60}
25	0.56	0.56	0.61	0.73	0.79
30	0.54	0.55	0.61	0.72	0.79
37	-	0.54	0.60	0.72	0.79
45	0.53	0.54	0.59	0.71	0.77

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and

$$\Delta\overline{S}_1 = R\phi_2{}^2(0.5 - \chi_S) \tag{12}$$

The partial molar free energy of dissolution is then given by:

$$\Delta\overline{G}_1 = RT\phi_2{}^2(\chi - 0.5) \tag{13}$$

According to the dependence of the partial molar quantities of dissolution with temperature, the AA/MMA hydrogels can be divided in two groups: those in which all the thermodynamic quantities decrease with increasing temperatures (AA100, AA90 and AA80) and in which $\Delta\overline{S}_1 > 0$ at all temperatures, and those (AA70 and AA60) in which $\Delta\overline{S}_1$ is negative and increases slightly with temperature, $\Delta\overline{H}_1$ is always positive and also increase slightly with temperature whereas $\Delta\overline{G}_1$ is positive but it does not depend significantly on temperature. Moreover, the magnitudes of $\Delta\overline{G}_1$, $\Delta\overline{H}_1$ and $\Delta\overline{S}_1$ are much larger with AA70 and AA60 samples. These two behaviors are illustrated in Table 4 for the AA90 and the AA60 hydrogels.

Table 5 shows that the swelling of hydrogels is unfavorable even for the hydrophilic AA100 ($\Delta\overline{G}_1 > 0$) and becomes more unfavorable as the amount of MMA content in the hydrogels increases as indicated by the large increase in $\Delta\overline{G}_1$ from AA100 to AA60. This behavior is clearly related to the decrease of the hydrophilic acrylic acid units which bind more strongly with water molecules

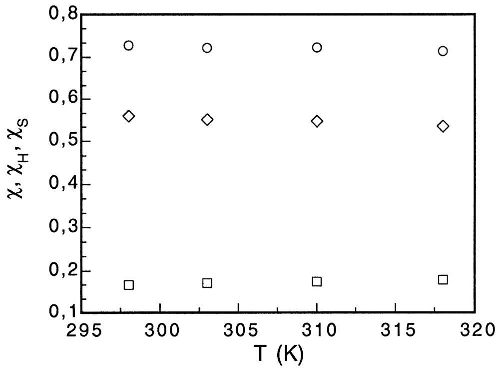

Figure 2. Plot of the interaction parameter (○) and its entropic, χ_S, (◇) and enthalpic, χ_H, (□) contributions for AA70 hydrogel.

TABLE 4. Partial Molar Free Energies ($\Delta\overline{G}_1$), Enthalpies ($\Delta\overline{H}_1$) and Entropies ($\Delta\overline{S}_1$) of Dissolution as a Function of Temperature for the AA90 and AA60 Hydrogels

T (°C)	$\Delta\overline{G}_{1\,AA90}$ J/mol	$\Delta\overline{G}_{1\,AA60}$ J/mol	$\Delta\overline{H}_{1\,AA90}$ J/mol	$\Delta\overline{H}_{1\,AA60}$ J/mol	$\Delta\overline{S}_{1\,AA90}$ J/mol·K	$\Delta\overline{S}_{1\,AA60}$ J/mol·K
25	4.246	193.6	24.48	142.0	0.068	- 0.173
30	2.288	194.0	17.13	145.3	0.049	- 0.161
37	1.341	197.0	12.70	151.6	0.037	- 0.147
45	1.215	184.1	12.46	151.8	0.035	- 0.101

and allows larger swellings. Both the enthalpic and entropic contributions become more unfavourable (which causes the increase in $\Delta\overline{G}_1$) as the hydrogels become more hydrophobic. The swelling process becomes more endothermic. i.e., $\Delta\overline{H}_1$ increasingly positive, as the content of MMA increases, because of the reduction of molecular interactions among the carboxyl groups and water. $\Delta\overline{S}_1$ decreases as the content of MMA in the hydrogels increases and eventually becomes negative, as a result of the decreasing interactions of water and the hydrogel, which leads to an increasing ordering of water molecules.

It is noteworthy that increasing the hydrophobic character of the hydrogel has a larger effect on the partial thermodynamic properties of dissolution than temperature (cf. Tables 4 and 5). Hence, the hydrophobic hydration and the hydrophobic interactions in the hydrogel prevail over temperature effects on hydrogen-bonding interactions among the water molecules and the hydrophilic groups. Moreover, the increase in $\Delta\overline{S}_1$ with temperature implies that bound water in the hydrogel tends to disarray.

TABLE 5. Partial Molar Free Energies ($\Delta\overline{G}_1$), Enthalpies ($\Delta\overline{H}_1$) and Entropies ($\Delta\overline{S}_1$) of Dissolution at 37°C for the AA/MMA Hydrogels

SAMPLE	$\Delta\overline{G}_1$ J/mol	$\Delta\overline{H}_1$ J/mol	$\Delta\overline{S}_1 . 10^{-2}$ J/mol·K
AA100	1.2	15.6	4.6
AA90	1.3	12.7	3.7
AA80	16.2	42.5	8.5
AA70	113.3	88.9	- 7.9
AA60	197.0	151.6	- 14.7

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In contrast to butyl acrylate (BA)/N-vinyl-2-pyrrolidone (VP) hydrogels, where the swelling process is exothermic ($\Delta\bar{H}_1$ = - 1600 J/mol) and $\Delta\bar{S}_1$ = - 9.3 J/mol·K at 342 K [13], the values of these thermodynamic quantities for the hydrogels examined here are much smaller and the swelling process is endothermic, particularly at high contents of MMA. $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ of the AA100 are comparable, although opposite in sign, to those of the hydrophilic poly(N-vinyl-2-pyrrolidone) hydrogels ($\Delta\bar{H}_1$ = - 0.92 J/mol and $\Delta\bar{S}_1$ = - 0.044 J/mol·K at 342 K) [17].

Freezing and Non-Freezing Water Content

When water is constrained in nanoscopic structures and porous media such as liquid crystals and glass filters, at least three different types of water have been detected [21-23]: bulk-like water, which has similar properties to bulk water, interfacial water, which is weakly bound and exhibits a melting transition between 268 and 271 K, and bound water, which is strongly bound and whose melting transition can not be detected at temperatures as low as -100°C. Lee *et al.* [24] and Kim *et al.* [25] have also proposed the existence of at least three distinct forms of water in PHEMA hydrogels. Nevertheless, only freezing water (free water) and non freezing water (bound water) are commonly reported by DSC [13, 17]. The physicochemical properties of a hydrogel depend not only on molecular structure, gel structure, degree of crosslinking and water content, but also on the relative concentrations of free and bound water [26].

Figure 3 shows a typical thermogram of the hydrogels studied. Upon heating, the onset of the melting transition of water is detected at temperatures as low as -20°C and it appears to be the superposition of two peaks. In cooling scans, supercooling of water shifts the crystallization transition to temperatures below -20 and down to -40°C. Again, the crystallization transition of water appears to be the superposition of two peaks. Bulk water usually supercools to temperatures around -15 to -20°C. However, interfacial water can supercool to temperatures as low as -50°C [23]. Evidently, DSC thermograms reveal the presence of at least two types of water, bulk-like and interfacial water. However, we were unable to split these two peaks by DSC even by decreasing the heating and cooling rates to values as low as 1ºC/min. Ahmad *et al.* [27], on the other hand, observed two well resolved water crystallization peaks in hydrogels of poly(MMA-co-VP) only when the cooling rate was 2.5°C/min or lower.

The estimated values of W_f and W_{nf} are reported in Table 6 as a function of hydrogel composition. Here, one can see that the content of free water

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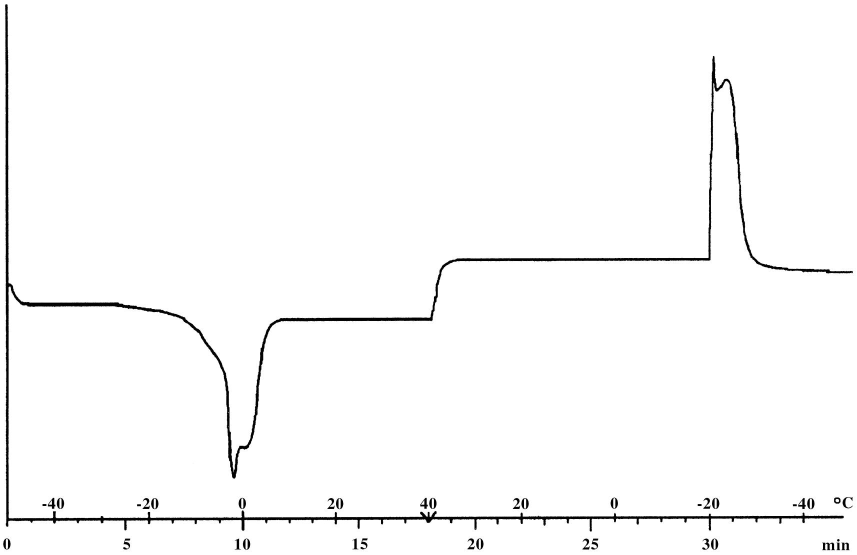

Figure 3. DSC thermogram for a hydrogel sample.

decreases as the MMA content in the hydrogels increases whereas the content of bound water follows the opposite trend. Notice also that the ratio of bound to total water (W_{nf}/W) increases as the swelling of the hydrogels decreases because the number of water molecules surrounding the hydrophobic units (hydrophobic hydration effect) should increase with increasing concentration of MMA units in the hydrogel (Table 6). Similar behavior was reported by Higuchi and Ligima [28] and Davis *et al.* [17] Notice also that the hydrogels become more and more rigid as the content of free water decreases (cf. Tables 2 and 6).

The ratio W_{nf}/W versus temperature for all the AA/MMA hydrogels studied is shown in Figure 4. Regardless of composition, W_{nf}/W decreases with

TABLE 6. Percentage of Total, Free and Bound Water Normalized with Respect to Weight of Hydrogel in the AA/MMA Hydrogels at 37°C.

SAMPLE	W (%)	W_f (%)	W_{nf} (%)	W_{nf}/W_f
AA100	86.7	74.44	12.26	0.142
AA90	85.8	73.55	12.22	0.143
AA80	71.7	58.46	13.24	0.184
AA70	55.3	39.63	15.67	0.284
AA60	48.0	30.12	17.88	0.373

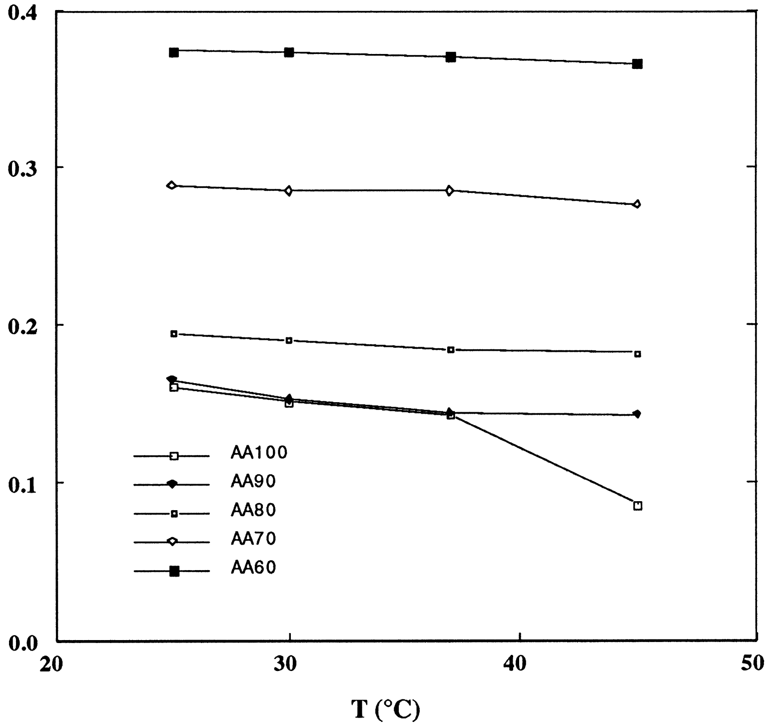

Figure 4. Ratio, W_{nf}/W, of nonfreezing to total water as a function of temperature for the AA/MMA hydrogels.

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increasing temperature for all the hydrogels. This is because the total number of water molecules forming cage-like structures around the hydrophobic MMA units, diminishes with increasing temperature, promoting then, hydrophobic interactions [29]. With AA100, on the other hand, W_{nf}/W decrease more rapidly because hydrogen bonding interactions also decreases with increasing temperature.

CONCLUSION

The mechanical and thermodynamic properties of AA/MMA hydrogels were examined as a function of composition. We found that the swelling capacity of the hydrogels and the elasticity increase as the degree of hydrophilicity increases, i.e., in the order AA60 to AA100. The increase in swelling capacity with temperature is faster with the more hydrophilic AA100 hydrogel. From measurements of swelling capacity and mechanical properties as function of temperature, the thermodynamic properties were estimated. The swelling process is unfavourable and more endothermic as the degree of hydrophobicity increases. In all cases, $\Delta\overline{G}_1 > 0$ and $\Delta\overline{H}_1 > 0$. The partial molar entropy of dissolution reflects the increasing ordering of water as the degree of hydrophobicity increases. This is also reflected in the increase of the ratio of non-freezing water to total water (W_{nf}/W_f) as the amount of MMA in the hydrogels increases.

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