

# Effect of Crosslinking Concentration on Mechanical and Thermodynamic Properties in Acrylic Acid-co-Methyl Methacrylate Hydrogels

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**ABSTRACT:** The mechanical and thermodynamic properties of poly(acrylic acid-co-methyl methacrylate) hydrogels with varying crosslinker *N,N'*-methylenebisacrylamide (NMBA) content are reported. A higher NMBA content generally led to a stronger and harder gel with lower water content. Swelling capacity decreased as the NMBA concentration increased between 0.5% and 2%, remaining constant beyond this range. The temperature changes of the partial molar Gibbs free energy of dilution and enthalpic and entropic contributions were examined. The thermodynamic parameters showed that swelling was an unfavorable and endothermic process. The freezing and

nonfreezing water in the hydrogel was determined by differential scanning calorimetry (DSC). Freezing water content decreased with increasing crosslinker (NMBA) content, whereas the ratio of nonfreezing water to total water content increased with NMBA content because of the promoting of hydrophobic interactions in the hydrogels. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4016–4022, 2006

**Key words:** hydrogels; poly(acrylic acid-co-methyl methacrylate); crosslinking density; hydrophobic interaction; *N,N'*-methylenebisacrylamide

## INTRODUCTION

Hydrogels are water-swallowable three-dimensional polymeric networks and have been attracting a lot of attention because they are functional polymers that have water absorption properties<sup>1–3</sup> that determine the functionality and quality of the hydrogel. The absorption of water by a hydrogel is one of the most important factors that determines its properties and applications. The behavior of highly swollen hydrogels is a function of network characteristics such as equilibrium degree of swelling, crosslink density, and diffusion parameters that are intimately related to the chemical structure of the hydrogel.

Hydrogels have received significant attention, especially in the last 30 years, because of their potential applications in many areas.<sup>4</sup> We previously reported on acrylic acid copolymerized with different methacrylate monomers.<sup>5</sup> This and other copolymeric systems have been used as possible matrices for drug release. Usually large swelling is accompanied by decreased mechanical strength. For many applications, a combination of large swelling and good mechanical properties is very important. A number of approaches have

been used to improve the mechanical properties of hydrogels, including copolymerization of hydrophilic monomers with hydrophobic ones, increasing crosslinking density, and varying polymerization conditions.<sup>6–9</sup> Properties of a hydrogel depend not only on molecular structure, degree of crosslinking, and water content, but also on the relative concentration of free and bound water.<sup>10</sup> There is a great deal of evidence that water in polymers can exist in more than one state, thus affecting the properties of the polymers. Water in a polymer network exists in continuous states between two extremes, such as water strongly associated with a polymer network through hydrogen bonding, also called bound, or nonfreezing, water, and water with high mobility, referred to as freezing water.<sup>11</sup> The ratio of freezing to nonfreezing water has a strong influence on the properties of the hydrogels.

In this work we investigated the influence of crosslinking content on the swelling capacity as well as the mechanical and thermodynamic properties of poly(acrylic acid-co-methyl methacrylate) hydrogels with varying crosslinking content (NMBA). We studied the structure of water in these hydrogels, too.

## 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

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(MMA) from Polyscience was used as received. *N,N'*-Methylenebisacrylamide (NMBA) with a purity of 98% (Fluka) was further purified by recrystallization from methanol. Pure 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50) was purchased from Wako. It was further purified by recrystallization from methanol. Doubly distilled deionized water drawn from a Millipore Milli-Q water purification system was used for the swelling and DMA tests.

### Polymerization

Hydrogels of acrylic acid/methyl methacrylate monomers of composition 90/10% by volume were prepared by radical crosslinking polymerization, varying crosslinking amounts in order to obtain 0.5%, 1%, 2%, 3%, and 4% with respect to the total monomers. The mixture of the monomers were degassed prior to polymerization. Quantities were prepared as follows: the appropriate amount of *N,N'*-methylenebisacrylamide (NMBA) was dissolved in 6 mL of ethanol and poured into a 10 mL test tube containing the monomer mixture. Then 0.004 g of 2,2'-azobis(2-amidinopropane) dihydrochloride were dissolved in 1 mL of water and added to the test tube to initiate the reaction. The contents of both tubes were purged with nitrogen for 10 min and then mixed. Polymerization reactions were carried out at 50°C for 6 h. The resulting hydrogels were cut into a disk and immersed in ethanol and then in water for 7 days to remove the unreacted monomers and soluble materials.

### Swelling studies

Xerogels were obtained by drying the gels at room temperature for 1 week and then in an oven at 40°C until a constant weight was reached. The disk of xerogel was shaped by cutting (diameter ~ 9 mm, thickness ~ 1 mm), weighed ( $m_0$ ), and immersed in excess deionized water until equilibrium swelling was achieved at 298, 303, 310, and 318 K. The water content at equilibrium or equilibrium swelling,  $W$ , was calculated by:

$$W(\%) = 100 \frac{m_f - m_0}{m_0} \quad (1)$$

where  $m_f$  and  $m_0$  are the weights of the swollen gel at equilibrium swelling and the xerogels, respectively. At least four measurements were made of swelling at equilibrium, and averages were calculated.

The volume fraction of polymer within the hydrogel,  $\phi_2$ , at a particular temperature was calculated by:

$$\phi_2 = (D_0/D)^3 \quad (2)$$

where  $D_0$  and  $D$  are the diameters of the dry and equilibrium swollen disks, respectively. The dimensions of the xerogel were measured with a micrometer.

### Compression measurements

A Perkin Elmer DMA-7 dynamic mechanical analyzer with parallel plate geometry was used for compression strain-stress testing. The compression-stress measurements were performed in a manner similar to that employed by others in the determination of network parameters for a series of hydrogels.<sup>12,13</sup> The xerogel samples were allowed to equilibrate for 4 weeks in deionized water. The initial slope of the stress-strain curve was measured for each sample. An average was computed from four measurements for each formulation. Young and compression modules of the hydrogels were determined in the compression mode. Deionized water was used to immerse the hydrogel disks during measurements. A stainless-steel parallel plate kit with a 20-mm diameter and a cup accessory to contain water throughout the measurement and minimize water loss was used.

The effective crosslink density,  $\nu_e$ , of the swollen gels was obtained from compression-strain measurements using the following relationships:<sup>1</sup>

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

$$G = RT\nu_e\phi_2^{-1/3}(\nu_u/\nu_f)^{2/3} \quad (4)$$

where  $\tau$  is the applied force per unit area of the xerogel and  $\lambda$  is the ratio of the deformed to undeformed lengths of the hydrogel. Over the range of strain covered, from 0 to -0.07, the plots were linear. The reversibility of the gel deformation was also checked by several samples and found to be reversible. The values of effective crosslink density,  $\nu_e$ , were derived from the slopes of the linear plots of stress,  $\tau$ , versus  $(\lambda - \lambda^{-2})$ , according to eq. (3) and the use of eq. (4), in which,  $V_u$  is the volume of dried, unstrained gel and  $V_f$  the volume of the network at formation.  $RT$  has its normal meaning.<sup>14,15</sup>

The parameter usually employed to characterize crosslinked polymer samples (such as hydrogels) is the molar mass between crosslink ( $M_C$ ). According to the theory of rubber elasticity, the elastic modulus permits the calculation of the mean molar mass between crosslinks of the elastically active chains,  $M_C$ , as:

$$M_C = \rho RT/G \quad (5)$$

where  $G$  is the shear modulus in the elastomeric region,  $\rho$  is the density of the xerogel obtained from the weight and volume,  $R$  is the gas constant, and  $T$  is the absolute temperature.

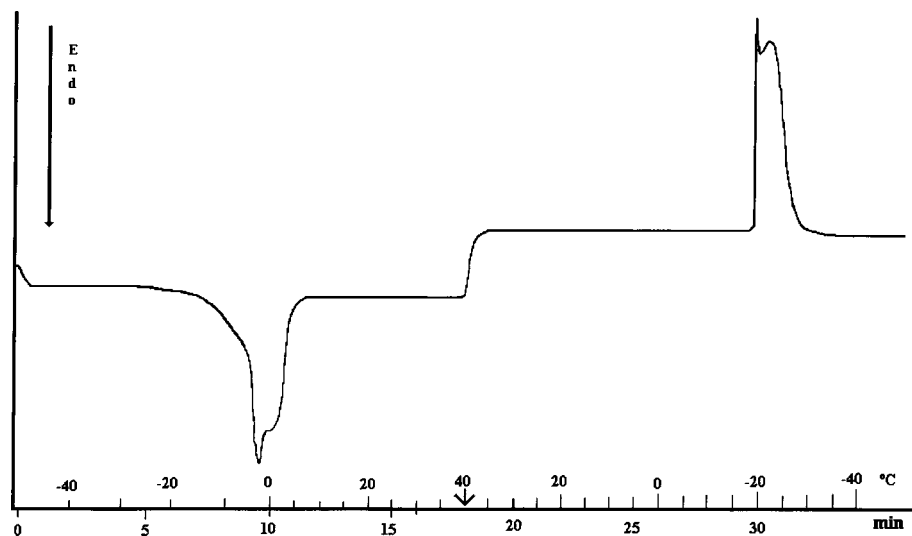


Figure 1 DSC thermogram of swollen poly(acrylic acid-co-methyl methacrylate) (AA90/MMA10) gel with 1% NMBA.

### Differential scanning calorimetry

Thermograms were obtained in a Mettler TA4000 differential scanning calorimeter equipped with a refrigeration unit. Excess water was removed by tapping the surface of the hydrogels with filter paper. Samples were cooled to 223 K to ensure that all the water was frozen. The samples were then heated at a rate of 1°C/min to ambient temperature. In general, the state of water in a hydrogel can be differentiated into free and frozen-bound water. Free water is water that does not form any hydrogen bonds with the hydrogel. It exhibits a transition temperature, enthalpy, and DSC curve similar to those of pure water. Frozen-bound water, also known as bound water, has water molecules that are bound to the polymer segments of hydrogel through hydrogen bonds. This type of water shows no endothermic peak in the temperature range from  $-50^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ . The free water was estimated from the measured enthalpy of the water peak obtained from the area of the melting transition and the value reported in the literature (321.17 J/g).<sup>16</sup> The amount of frozen-bound water (bound water) in the hydrogels was calculated by the difference from the total water content. The weight ratio of free water and bound water to the total weight of the equilibrium swollen hydrogel was denoted as  $W_f$  and  $W_b$ , respectively. Figure 1 shows the DSC thermogram of one of the studied poly(acrylic acid-co-methyl methacrylate) hydrogels. Two melting peaks can be seen in the DSC curves of poly(acrylic acid-co-methyl methacrylate) (AA90/MMA10) hydrogels, indicating that free and frozen-bound water exist in the gel.

The volumes of free and bound water were calculated from the melting enthalpies. The following equation assumed that the heat of fusion of free water in the hydrogel was the same as that of ice:

$$W_b(\%) = W(\%) - W_f(\%) \\ = W(\%) - (Q_{\text{endo}}/Q_f) \times 100 \quad (6)$$

where  $W_b$  is the volume of bound water (%),  $W_f$  is the volume of free water, and  $Q_{\text{endo}}$  and  $Q_f$  are the heats of fusion of free water in the hydrogel and the ice (321.17 J/g), respectively.

## RESULTS AND DISCUSSION

### Swelling behavior

Table I summarizes the swelling properties of the AA90/MMA10 hydrogels for five concentrations of NMBA in the range of 0.5%–4% relative to total monomer content. The effect of the concentration of the crosslinking agent in the hydrogel composition showed two dependence patterns. Equilibrium swelling decreased as the NMBA concentration increased from 0.5% to 2% and then remained constant beyond that range. A higher NMBA content generally led to a stronger and harder gel with a lower water content. This was expected because of the decreasing mesh size of the network with increasing crosslinker den-

TABLE I  
Equilibrium Swelling,  $W$ , and Volume Fraction of Polymer,  $\phi_2$ , Measured at 298 K for AA90/MMA10 Hydrogels as a Function of NMBA Content

NMBA (%)	$W$ (%)	$\phi_2$
0.5	90.5	0.079
1	77.9	0.169
2	71.6	0.250
3	71.9	0.250
4	72.1	0.248

**TABLE II**  
Network Parameters at 298 K for Poly(AA-co-MMA) Hydrogels Prepared with Different NMBA Contents

NMBA (%)	$E$ (MPa)	$G$ (MPa)	$v_e \times 10^3$ (mol/dm <sup>3</sup> )	$M_C$ (kg/mol)	$\chi$
0.5	0.10	0.034	5.9	223	0.52
1	0.20	0.067	14.9	81	0.56
2	0.31	0.105	26.7	49	0.60
3	0.29	0.096	24.4	53	0.60
4	0.30	0.099	25.1	51	0.60

sity, which limited the diffusion of water molecules into the gel network. The insensitivity to change in water content with an NMBA content higher than 2% was probably a result of the lower reactivity of this crosslinking agent to water. Low crosslinking efficiency of NMBA in acrylic hydrogels was demonstrated previously.<sup>17</sup>

The effects of the concentration of the crosslinking agent in the hydrogel on the network parameters are shown in Table II. In the 0.5%–2% range, an increase crosslinking agent content enhanced hydrophobic bonding and, consequently, the effective crosslink density. A Young modulus increase leads to a decrease in  $M_C$  according to the statistical theory of rubber elasticity. Elastic behavior in the first region was expected with increasing crosslinker content, as shown in Table I; swelling remained at its limiting value. For an NMBA content higher than 2%, these values were independent of the crosslinking content used in the synthesis. It has been pointed out that greater dilution of monomers, the hydrogels in the present study, leads to a reduction in crosslinks when introduced simultaneously with the polymer main chain but also overshadows the effects of crosslinks and other controlling factors.<sup>18</sup> When the monomer concentration in formulations is low, the existence of a large pore volume induces macroscopic inhomogeneities.<sup>19</sup>

Table II also reports the values of the polymer solvent interaction parameter,  $\chi$ , which represents the specific interaction between water and polymers calculated from the Flory–Rehner equation<sup>20</sup>

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 + v_e V_1 \left( \phi_2^{1/3} - 2 \frac{\phi_2}{f} \right) = 0 \quad (7)$$

where  $V_1$  is the molar volume of water ( $18.05 \times 10^{-3}$  dm<sup>3</sup>/mol, at 298 K)<sup>19</sup> and  $f$  is the functionality of crosslinker (for NMBA, tetrafunctional,  $f = 4$ ). This expression is valid only at swelling equilibrium. The values of interaction parameters at four temperatures for the hydrogels synthesized with different quantities of NMBA are shown in Table III.

The interaction parameter represents the specific interaction between solvent and polymer system. Values of  $\chi > 0.50$  suggest that the solvent employed

is thermodynamically poor. All calculated  $\chi$  values exceeded 0.50 and decreased only slightly with temperature. An increase in NMBA content up to 2% led to an increase in  $\chi$ . This behavior can be explained by the relative hydrophobicity of the NMBA. The value of this parameter remained constant for an NMBA content larger than 2%. The total interaction parameter could be separated into two contributions: the entropic,  $\chi_S$ , and the enthalpic,  $\chi_H$ , according to the following equations:

$$\chi = \chi_H + \chi_S \quad (8)$$

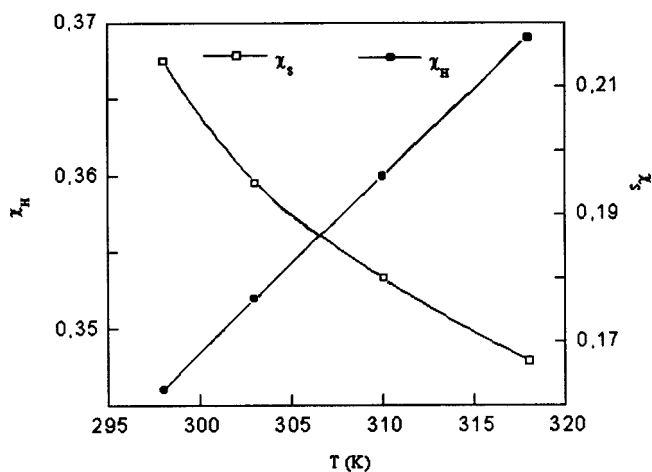
$$\chi_H = \chi + T(d\chi/dT) \quad (9)$$

$$\chi_S = \chi - T(d\chi/dT) \quad (10)$$

The dependence of  $\chi_S$  and  $\chi_H$  on temperature for the AA90/MMMA10 hydrogels containing 1% NMBA is depicted in Figure 2. For all the hydrogels studied,  $\chi_S$  was less than  $\chi_H$ . For a given NMBA content,  $\chi_S$  decreased as temperature increased, whereas  $\chi_H$  showed the opposite behavior. The enthalpic parameter was positive for all temperatures and NMBA contents. At a given temperature  $\chi_H$  increased with NMBA content up to 3% and then decreased slightly. The entropic contribution decreased until an NMBA content of 3% and increased slightly for the highest NMBA content. On the other hand,  $\chi_S$  was positive for an NMBA content between 0.50% and 1% and was negative for an NMBA content up to 2% (see Fig. 3).

**TABLE III**  
Interaction Parameter as a Function of Temperature for AA90/MMA10 Hydrogels with Varying NMBA Content

% NMBA	$\chi_{AA90/MMA10}$			
	298 K	303 K	310 K	318 K
0.5	0.52	0.51	0.51	0.51
1	0.56	0.55	0.54	0.54
2	0.60	0.60	0.58	0.56
3	0.60	0.60	0.58	0.56
4	0.60	0.59	0.58	0.56



**Figure 2** Entropic and enthalpic contributions to the interaction parameter for AA90/MMA10 hydrogels with 1% NMBA.

The partial molar enthalpy,  $\overline{\Delta H}_1$  (J/mol), and entropy,  $\overline{\Delta S}_1$  (J mol<sup>-1</sup> K<sup>-1</sup>), of dissolution were calculated according to the following equations:

$$\overline{\Delta H}_1 = RT\phi_2^2\chi_H \quad (11)$$

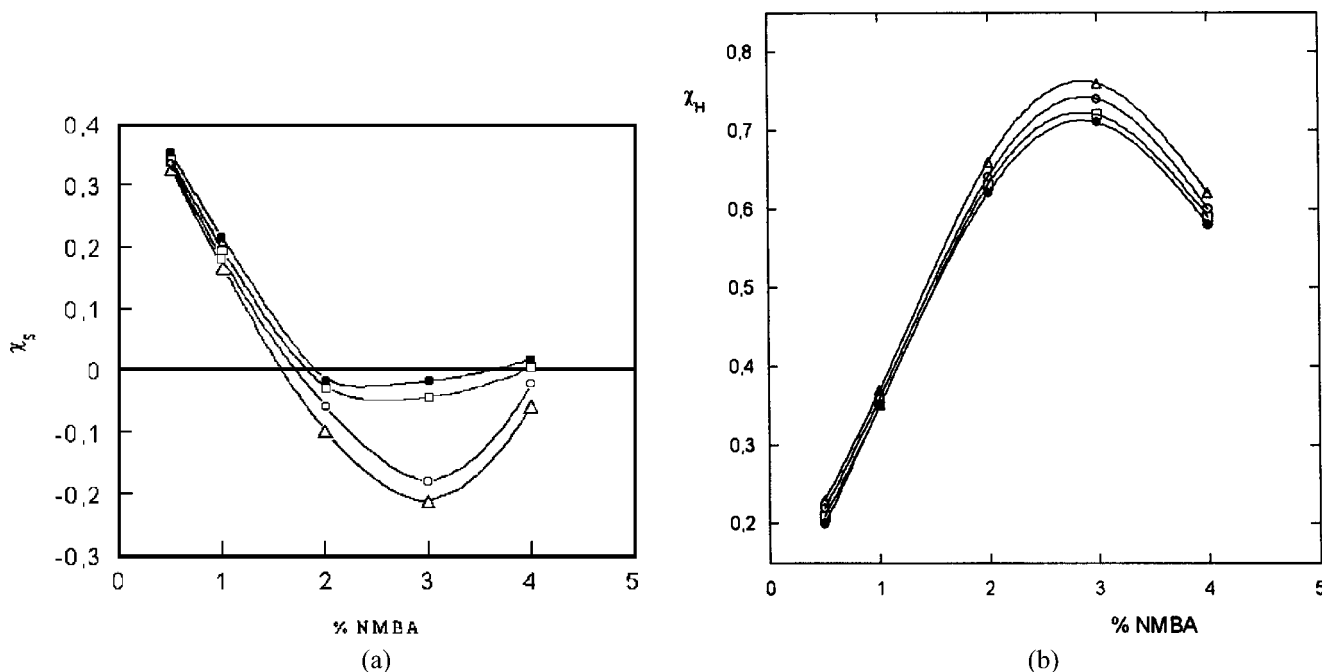
$$\overline{\Delta S}_1 = R\phi_2^2(0.50 - \chi_S) \quad (12)$$

The partial molar-free energy of mixing,  $\overline{\Delta G}_1$ , was then given by

$$\overline{\Delta G}_1 = RT\phi_2^2(\chi - 0.50) \quad (13)$$

The changes in thermodynamic magnitude with temperature and NMBA content are listed in Table IV, which showed the following features:  $\overline{\Delta H}_1$ ,  $\overline{\Delta S}_1$ , and  $\overline{\Delta G}_1$  were positive over the entire temperature range and were highest at the lowest temperature; all thermodynamic quantities decreased with increasing temperature; positive values of  $\overline{\Delta G}_1$  indicated swelling of the AA90/MMA10 hydrogels was an unfavorable thermodynamic process; and a positive enthalpic contribution produced  $\overline{\Delta G}_1$  values greater than zero. When temperature was increased, the process was more favored enthalpically, but this contribution remained positive, and thus, the overall process was unfavorable. In addition, the decreases in and positive values of the partial molar entropy free of dissolution with temperature contributed to the positive  $\overline{\Delta G}_1$ .

Table IV shows that for a given temperature, the thermodynamic magnitude was positive for all the hydrogels studied and increased with NMBA content up to 2%. The swelling of hydrogels was unfavorable even for the most hydrophilic hydrogel, that is, the hydrogel with the smallest crosslinker content (0.5%), and became more unfavorable as the NMBA content of the hydrogels increased from 0.5% to 2%, as indicated by the large increase in  $\overline{\Delta G}_1$ . The increase in entropy could be a result of water in the vicinity of the network groups, which prevented the formation of a hydrophobic interaction. This should have produced a more favorable swelling process. However, the enthalpic contribution, which became more unfavorable (increasingly positive) as the hydrophobic charac-



**Figure 3** Variation in the (a) entropic (a) and (b) enthalpic contributions with NMBA content at different temperatures: (●) 298 K, (□) 303 K, (○) 310 K, (△) 318 K.

ter of the hydrogels increased, counteracted the small entropic contribution. The swelling process was then more endothermic. This behavior was clearly related to the weak binding to water molecules, allowing for poorer swelling. For higher NMBA contents, these values were positive and much larger, but did not depend significantly on NMBA content, as expected from the swelling behavior.

### Freezing and unfreezing water content

The peak temperatures were between 275 and 278 K in every sample. The thermograms show that both total equilibrium water content and free water content decreased with increasing NMBA content up to 2%. These results indicate that the degree of crosslinking increased with increasing NMBA content. An increase in crosslinking content produced a large decrease in free water content up to 2% NMBA and remained constant for higher NMBA contents. The  $W_f$  and  $W_{nf}$  values are reported in Table V as a function of NMBA content.

The ratio of nonfreezing water to total water increased as the swelling of hydrogels decreased until 2% because of the hydrophobic hydration effect, and the number of water molecules around hydrophobic units should have increased with an increasing concentration of NMBA in the hydrogel. The effect of crosslink density on total water content and freezing water content followed the expected trend, with both decreasing when crosslink density increased.

**TABLE IV**  
Partial Molar Free Energy ( $\Delta G$ ), Enthalpy ( $\Delta H$ ), and Entropy ( $\Delta S$ ) of Dissolution as a Function of Temperature for AA90/MMA10 hydrogels

T (K)	NMBA (%)	$\Delta G$ (J/mol)	$\Delta H$ (J/mol)	$\Delta S$ ( $\times 10^2$ ) (J mol <sup>-1</sup> K <sup>-1</sup> )
298	0.5	0.33	2.63	0.8
	1	4.26	24.48	6.8
	2	15.33	95.54	26.9
	3	13.42	101.61	29.6
303	0.5	0.14	1.73	0.5
	1	2.28	17.13	4.9
	2	15.06	96.52	26.9
	3	8.97	81.20	23.8
310	0.5	0.08	1.38	0.4
	1	1.34	12.70	3.7
	2	9.71	76.07	21.1
	3	4.24	53.26	15.8
318	0.5	0.06	1.25	0.4
	1	1.22	12.46	3.5
	2	4.30	48.01	13.7
	3	2.37	38.27	11.3
	4	4.53	46.67	13.3

**TABLE V**  
Percentages of Total, Free, and Bound Water Normalized with Respect to Weight of Hydrogel in AA90/MMA10 Hydrogels as Functions of Temperature and NMBA Content

T (K)	% NMBA	W (%)	$W_f$ (%)	$W_b$ (%)	$W_b/W$
298	0.5	90.5	83.4	7.1	0.08
	1	77.9	65.0	12.9	0.16
	2	71.6	58.4	13.2	0.18
	3	71.9	58.8	13.1	0.18
303	0.5	94.6	88.1	6.5	0.07
	1	82.0	69.6	12.4	0.15
	2	72.9	59.7	13.2	0.18
	3	73.1	59.9	13.2	0.18
310	0.5	96.2	90.2	6.0	0.06
	1	85.8	73.6	12.2	0.14
	2	74.9	61.9	12.3	0.17
	3	75.3	62.4	12.9	0.17
318	0.5	97.1	91.3	5.8	0.06
	1	86.9	74.5	12.4	0.14
	2	78.7	65.8	12.9	0.16
	3	79.2	66.4	12.8	0.16
	4	78.8	65.9	12.9	0.16

An increase in crosslinking density decreased the mobility and hydrophilicity inside the network. The bound water content remained nearly constant except for the hydrogels containing 0.5% NMBA, which were considerably higher. An increase in the number of crosslinks prevented the formation of new hydration shells. Some authors have pointed out that the percentage of bound water decreases when crosslinking hydrophilicity increases.<sup>21</sup> This suggests that in the hydrophilic networks most of the water absorbed by molecules only filled empty holes or microvoids in the polymer matrix and that no chemical bonds with polymer chains occurred.

The reduction in the total equilibrium water content was attributed only to loss of free water, except for hydrogels with 0.5% NMBA content, which lost both types of water. Corkill et al.,<sup>22</sup> using the concept of a hydration shell, pointed out that it is possible to entertain unfreezing water hydrogen bonded to the hydrophilic sites (hydroxyl groups) in the polymer chain with other hydration shells of freezing water molecules surrounding the inner hydration shell. As the number of monomer units between crosslinks ( $M_c$ ) decreases, the network becomes more tightly bound, and there is a marked decrease in freezing water content,  $W_f$ . This consideration seems adequate for the hydrogel system studied.

### CONCLUSIONS

The mechanical and thermodynamic properties of AA90/MMA10 hydrogels were examined as a function

of temperature and NMBA content. We found that the swelling and elastic properties of hydrogels increase up to 2% because of the increasing crosslinker concentration. An increase in the content of crosslinking agent produced a decrease in the effective crosslink density, and the Young modulus increased, leading to a decrease in  $M_C$ .

The thermodynamic properties were estimated as a function of temperature. We found that for a given NMBA content,  $\chi_S$  decreased as temperature increased, whereas  $\chi_H$  showed the opposite behavior. The swelling was an unfavorable and endothermic process.

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