Fluorocarbon-Containing Hydrophobically Modified Poly(acrylic acid) Gels: Gel Structure and Water State

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ABSTRACT: A series of hydrophobically modified poly(acrylic acid) gels (HM-PAA gels) were prepared by radical copolymerization of acrylic acid and a small amount of hydrophobic comonomers, 2-(*N*-ethyl perfluorooctane-sulfonamido)ethyl methacrylate and lauryl acrylate, respectively, in *tert*-butanol. The effects of hydrophobic modification on the structure and water state in hydrogels were studied by atomic force microscopy, differential scanning calorimetry, and thermogravimetric analyses. Significant differences in the enthalpy of dissociation of water per molar polymer unit were found between unmodified gel and hydrophobically modified gels (HM gels). Three states of water molecules—free water, nonfreezing water, and freezing bound water—were proven to exist in HM gels. The number of nonfreezing and freezing bound water molecules associated with a polymer unit, n_0 and n_1, increased with the hydrophobe content and the hydrophobicity of the hydrophobes. The roles of these water molecules are discussed in relation to hydrophobic association. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1258–1265, 2003

Key words: hydrogel; hydrophobic association; AFM; water state

INTRODUCTION

Hydrophobic associations in aqueous media have long been recognized.[1] Recently, some attention has been paid to the hydrophobic associations of hydrophobically modified gels (HM gels) that have a small number of hydrophobic side groups in their chain backbones.[2] These reports on focused mainly on hydrocarbon group–grafted or end-capped HM gels.[2] However, few articles can be retrieved about fluorocarbon-modified gels.[3] In our previous articles,[4–6] we reported on the synthesis,[4] rheological properties,[4,5] and fluorescence measurements of hydrophobically modified water-soluble polymers (HMWSPs).[6] Results showed that in HMWSPs fluorocarbon hydrophobes exhibited a much stronger association than did their hydrogenated counterparts, a result of their low-cohesive-energy density and surface energy. Therefore, we have explored the hydrophobic association of fluorocarbon groups in hydrogels.

From investigation into the state and role of water, it is known that water in hydrogels generally can be classified into three distinctly different physical states: freezing water (namely, free water), nonfreezing water (namely, bound water), and freezing bound water.[7,8] It is essential to know the amounts of free and bound water because that gives useful physical insight into the mechanism of water transport within the system. For example, water state plays an important role in enzymatic catalysis,[9] membrane permeability,[10] and protein and enzyme activity.[11] The nature of the hydrophobic association directly affects the structure, states, and properties of water in hydrogels. Therefore, it is necessary to investigate the states of water in hydrophobically modified hydrogels in order to understand the relationship between the hydrophobic microstructure and the macroscopic properties of HM gels, especially for fluorocarbon-containing hydrophobically modified hydrogels.

In addition to the above methods for studying hydrophobic association in HM gels, atomic force microscopy (AFM) as a forcing tool to probe the surface morphology of gels has sparked tremendous interest since it was developed by Binning.[12] Recently, AFM was used to measure the phase transition of poly(*N*-isopropylacrylamide) (PNIPAM) gels in response to temperature.[13] However, it is a big challenge to test the surface morphology of hydrogels because of their weak mechanical strength and the special way in which they exist. Here, we report on the initial investigation into the hydrophobic modification of fluorocarbon-containing hydrophobically modified gels by AFM.

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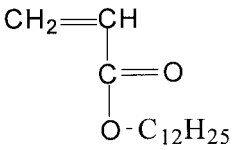
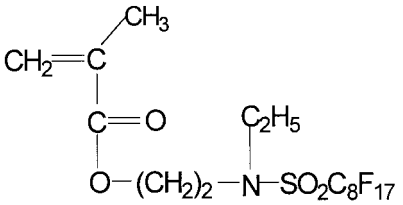


Lauryl acrylate (LA)



2-(N-ethylperfluorooctane-sulfoamido)ethyl methacrylate (FMA)

Scheme 1

Reported in this article are the results of a study in which a series of HM gels containing both physical and chemical crosslinking were synthesized by free-radical polymerization. The effects of hydrophobic modification on the structure and water state of gels were studied by AFM, thermogravimetric analyses (TGA), and differential scanning calorimetry (DSC).

EXPERIMENTS

Materials

Acrylic acid (AA) was distilled under vacuum before use. 2-(*N*-ethyl perfluorooctane-sulfonamido)-ethyl methacrylate (FMA), which was supplied by the 3M Company (USA), was recrystallized from methanol twice and dried under vacuum before use. Lauryl acrylate (LA) and diethylene glycol dimethacrylate (DEGDMA) were purchased from the Aldrich Company. Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. The chemical structures of two hydrophobic comonomers are depicted in Scheme 1.

Gel synthesis

The macroscopic hydrogels were prepared by radical copolymerization of acrylic acid (AA) with and without a specific amount of hydrophobic comonomer (FMA and LA) in *tert*-butanol. The fraction of the hydrophobic comonomer varied from 0.1 to 2.5 mol % (relative to moles of AA), whereas the concentration of AA remained constant at 2.2 mol/L. In all cases, AIBN (as initiator) was kept at 0.0011 mol/L and DEGDMA (as crosslinker) at 0.022 mol/L. The reaction was conducted in a sealed cylindrical glass tube (inner diameter = 10 mm) equipped with a nitrogen inlet tube at 60°C ± 0.5°C for 24 h. Polymerizations were carried out at high fractional conversions (90%) as indicated by the weight ratio of the dry gel to the initial total monomer.

The resulting gels were removed from the tubes and then soaked in a large amount of absolute ethanol, which was exchanged with fresh pure ethanol once every 2 days in order to remove all unreacted components. After at least 1 week the gels were dried in a vacuum oven at 40°C until their constant weight was obtained.

Characterization

Elemental analysis

The fluorocarbon content was determined by anion chromatography (Dionex 2110I). The component ratios, yields, and FMA conversion data of gels are listed in Table I.

Swelling measurement

The dry gel samples were immersed in excess pure water for 1 week. When gels were quickly removed, the surface water was carefully wiped off before weighing. Swelling capacity was recorded gravimetrically as:

$$\text{Swelling ratio } (SR) = (M_t - M_0)/M_0 \qquad (1)$$

where M_t and M_0 denote the weight of the swollen gels and the dry gels, respectively. All reported water contents are averages of at least three trials.

Thermogravimetric analyses

Dynamic thermogravimetric analyses (TGA) were carried out with a Perkin–Elmer TGA 7/DX system. All the thermogravimetric analyses were performed with 4–5 mg of finely cut sample pieces under a dynamic nitrogen atmosphere flowing at 50 mL/min. The experiments were run at a scanning rate of 3°C/min.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were carried out with a Perkin–Elmer Pyris-1. A piece of gel (about 3 mg) was crimped in a hermetically sealed aluminum DSC sample vessel. The temperature range was −40°C–60°C. The vessels were cooled first from room temperature to −40°C and then heated to 60°C at a heating rate of 3°C/min. The polymer concentration in a gel was adjusted by swell-

TABLE I
Component Feeds and Fluoroconversion in Syntheses of Gels[a]

Sample	Yield (wt %)	AA	LA	FMA	Actual[b] FMA/AA	FMA Conversion (%)
FMA–AA = 0.2	95	1	—	0.2	0.188	94
FMA–AA = 0.4	94	1	—	0.4	0.388	97
FMA–AA = 0.5	95	1	—	0.5	0.465	93
FMA–AA = 1.0	95	1	—	1.0	0.932	93
FMA–AA = 1.5	92	1	—	1.5	1.382	92
FMA–AA = 2.0	94	1	—	2.0	1.767	88
LA–AA = 0.2	91	1	0.2	—	—	—
LA–AA = 0.4	92	1	0.4	—	—	—
LA–AA = 0.5	92	1	0.5	—	—	—
LA–AA = 1.0	93	1	1.0	—	—	—
LA–AA = 1.5	92	1	1.5	—	—	—
LA–AA = 2.0	91	1	2.0	—	—	—

[a] In gel samples the feed amounts of monomer AA, chemical crosslinker EGDMA, and initiator AIBN were 2.2 mol/L, 0.022 mol/L, and 0.0011 mol/L, respectively.
[b] The F conversion was measured by anion chromatography.

ing the gel to the desired water content. The concentration was determined by weighing the gel before and after drying.

Atomic force microscopy

The microscopic image of the dry gel surface was determined by an atomic force microscope (AFM; Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) with a nanoprobe 200 μm in length and a pyramidal oxide-sharpened silicon nitride cantilever with a spring constant of 0.12 N m^{-1}. The opening angle of tip was 45°. The amplitudes used of the drive signal applied to the cantilever oscillation were in the range between 0.5 and 2 v. The scan rates ranged from 0.8 to 1 Hz. The images were recorded in the contact mode and processed only by flattening to remove background slope.

RESULTS AND DISCUSSION

Swelling properties

The various effects of the content of FMA on the equilibrium water uptake of the hydrophobically modified gels (HM gels) are presented in Figure 1. The equilibrium swelling ratios of the modified gels decreased significantly with the content of hydrophobes, which shows that a strong hydrophobic association that acts as physical crosslinking exists in HM gels. It is obvious that the swelling ratios of the FMA-modified gels were less than those of the LA-modified gels, although the length of LA chain (12C) was longer than that of the FMA chain (8C). This shows that fluorocarbon groups have a stronger ability for hydrophobic association than do the hydrocarbon groups in this prepared gel system. This result is consistent with our the results of our previous studies on HMWSP.[4]

Differential scanning calorimetry

According to the three-state water model in gels,[14] in the initial swelling process, water molecules first disrupt the intermolecular hydrogen bonds and then bind to the hydrophilic sites. These water molecules, which are isolated and uniformly distributed throughout the polymer, have greatly restricted mobility and are referred to as nonfreezing water (or bound water). Above a certain level of bound water, the additional water is preferentially oriented around the bound water and the polymer network structure as a secondary or tertiary hydration shell. These cagelike structures result from the tendency of water molecules to form

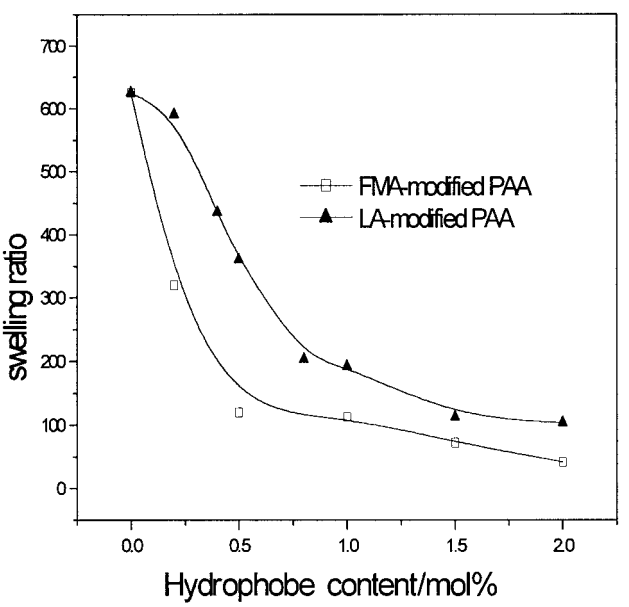


Figure 1 Dependence of the swelling ratios of hydrogels with different types of hydrophobes on the hydrophobe content.

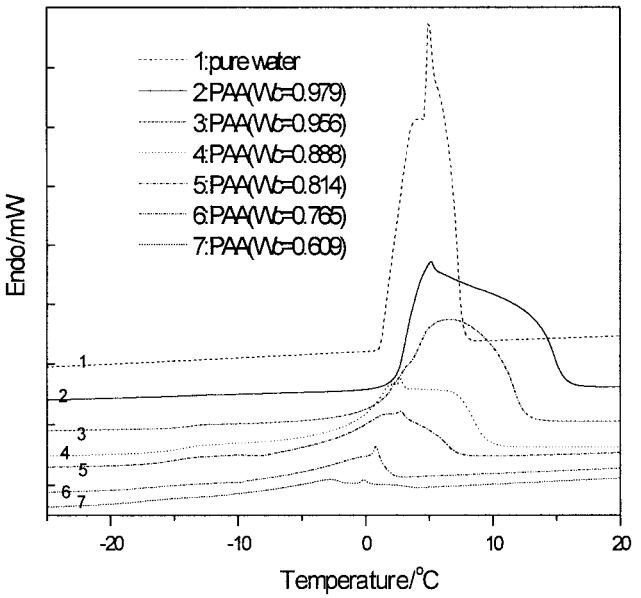


Figure 2 DSC curves of unmodified PAA gel with different water contents.

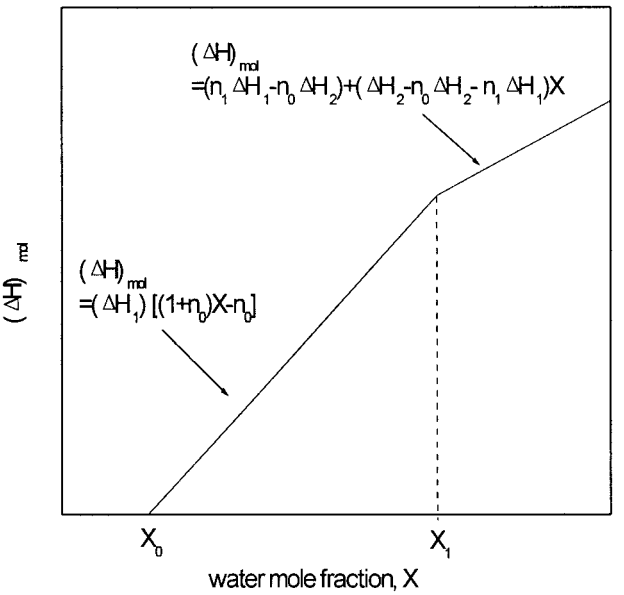


Figure 4 Schematic representations of $(\Delta H)_{mol}$ versus the water mole fraction, X.

the maximum amount of hydrogen bonds in the available space. This type of water is called freezing bound water. In gels the freezing bound water exhibits lower melting and higher freezing temperatures than the freezing water (free water).[7,14]

The corresponding differential scanning calorimetry (DSC) heating curves for samples PAA and FMA–AA = 1 with various water uptakes are shown in Figures 2 and 3, respectively. When the water content in the gels was above 0.700 (mol %), the DSC curves of the FMA-modified hydrogels exhibited two endothermic peaks, suggesting the existence of two states of freezing water (freezing bound water and freezing water). The peak at a lower temperature corresponded to the melting of freezing bound water. The magnitude of peak at a higher temperature corresponding to the melting of free water increased in height in proportion to the amount of water progressively added to the system. The splitting of the melting peak became more apparent in the DSC curves with a further increase of water uptake, suggesting that the freezing water portion became more and more predominant as the hydrogels gradually approached the equilibrium water uptake. No peaks are recorded on heating until the water content reached approximately 0.609 and 0.698

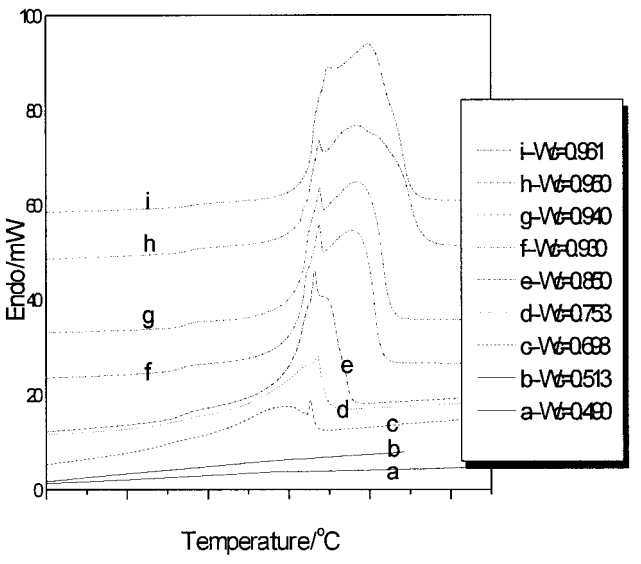


Figure 3 DSC curves of the gel sample FMA–AA = 1 with different water contents.

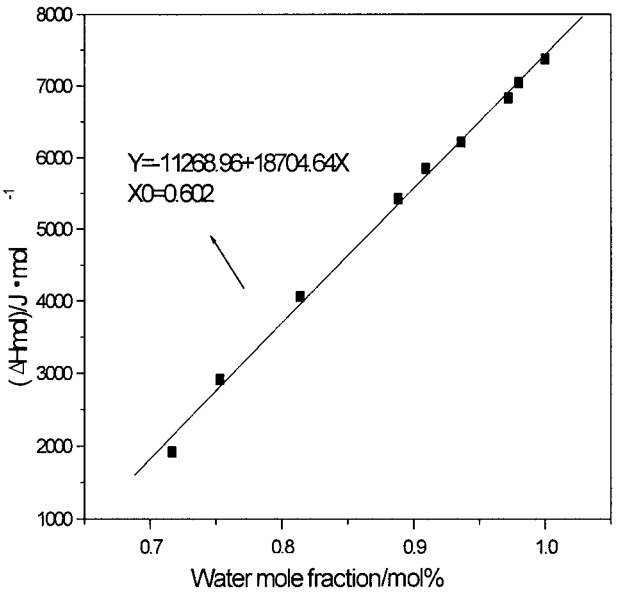


Figure 5 Dependence of $(\Delta H)_{mol}$ on the water content of the unmodified PAA gel.

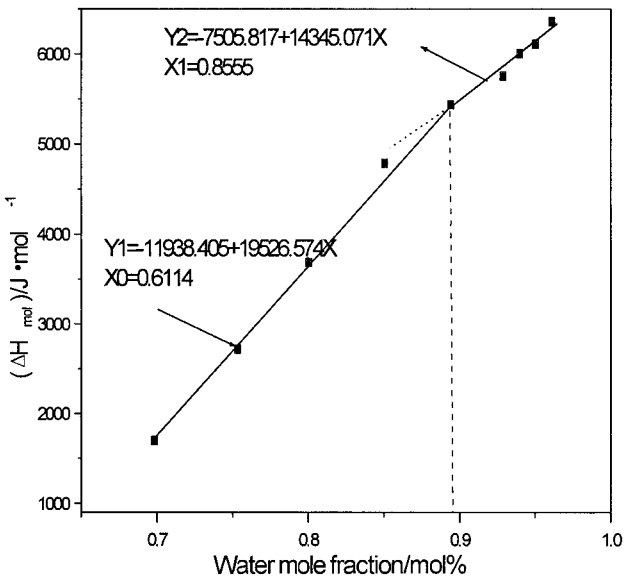


Figure 6 Dependence of $(\Delta H)_{mol}$ on the water content of the sample FMA–AA = 1.

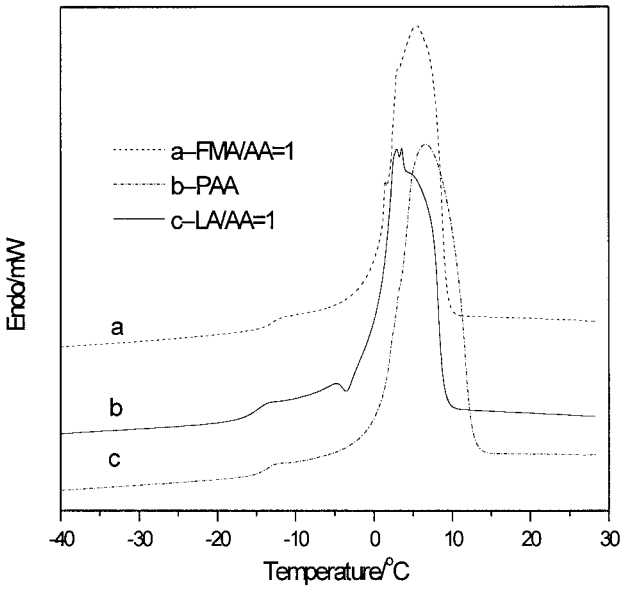


Figure 7 DSC curves of gels modified with different types of hydrophobes.

mol % for the PAA gel and FMA–AA = 1, respectively, indicating that nonfreezing water exists in these two kinds of hydrogels, that the amount of nonfreezing water in the sample FMA–AA = 1 was higher than in the unmodified PAA gel, and that the nonfreezing water content of FMA-modified gel was higher than that of the unmodified PAA gel.

To estimate the enthalpy of dissociation and the number of water molecules associated with polymer gels, we amended Shibayama's method.[15] Assuming that a gel polymer consists of x moles of water molecules and y moles of polymer units in the system and that the melting enthalpy of nonfreezing water is negligible, the enthalpy of dissociation for a gel–water system containing $(x + y)$ moles as the total, normalized by the total number of moles, $(\Delta H)_{mol}$, is given by

$$(\Delta H)_{mol} = \Delta H_1[X - n_0(1 - X)] = \Delta H_1[(1 + n_0)X - n_0] \quad X_0 \le X < X_1 \qquad (2)$$

$$(\Delta H)_{mol} = n_1 \Delta H_1(1 - X) + \Delta H_2[X - (n_0 + n_1)(1 - X)] = [n_1 \Delta H_1 - (n_0 + n_1)\Delta H_2] + [\Delta H_2(1 + n_0 + n_1) - n_1 \Delta H_1]X \quad X_1 \le X < 1 \qquad (3)$$

where X is the water mole fraction $[X = x/(x + y)]$; ΔH_1 and ΔH_2 are the enthalpy of melting of per mole of freezing bound water and of freezing water, respectively; and n_0 and n_1 are the stoichiometric numbers of nonfreezing water and freezing bound water per mole of polymer units.

Therefore, plotting $(\Delta H)_{mol}$ (obtained by DSC) as a function of X yields two lines, as shown in Figure 4. According to eqs. (1) and (2), the slopes of two lines, the intercept of the left line, and the abscissa of the crossing point of two lines, denoted by k_1, k_2, X_0, and X_1, respectively, are given by the following equations:

$$K_1 = \Delta H_1 (1 + n_0), \quad K_2 = \Delta H_2(1 + n_0 + n_1) - n_1 \Delta H_1), \qquad (4)$$

$$X_0 = n_0/(1 + n_0), \quad X_1 = (n_0+n_1)/(1 + n_0 + n_1) \qquad (5)$$

Shown in Figures 5 and 6 are, respectively, the areas under the DSC peaks as representing the changes in

TABLE II
Results of Linear Fit in Figures 5 and 6

Sample	k_1	k_2	n_0	n_1	X_0	X_1	ΔH_1 (J/mol)	ΔH_2 (J/mol)
PAA	18704.640	18704.640	1.513	0	0.6020	0	7443.15	7443.15
FMA–AA = 1	19526.574	14345.071	1.573	4.347	0.6114	0.8555	7589.03	6864.06

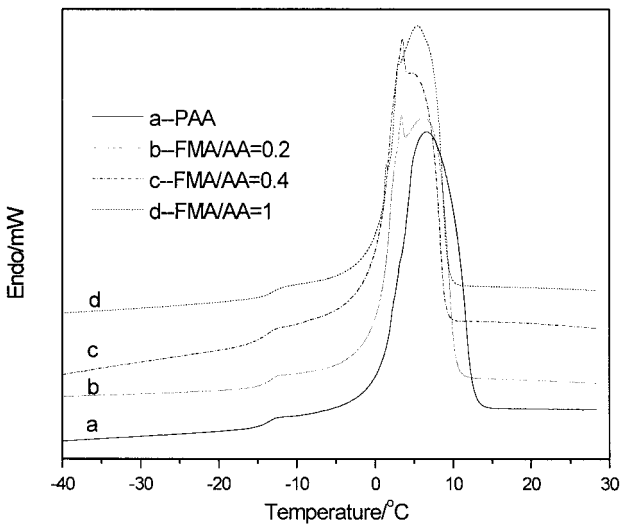


Figure 8 DSC curves of gels with different FMA contents.

enthalpy associated with the melting of water and plotted as a function of water uptake. As predicted by eqs. (1) and (2), the data points of the DSC experiments fit well with the linear function. The values of k_1, k_2, n_0, n_1, ΔH_1, and ΔH_2 of the unmodified PAA and the sample FMA–AA = 1 are listed in Table II.

As shown in Figure 6, a noticeable inflection can be found in the regression line of the DSC data, indicating the existence of freezing bound water in the sample FMA–AA = 1. In addition, for the sample FMA–AA = 1, ΔH_1 is obviously higher than ΔH_2 (shown in Table II), substantiating that freezing bound water has a higher enthalpy than does freezing water. However, no noticeable inflection can be found in the regression line of the unmodified PAA gel (Fig. 5), indicating a small amount of freezing bound water.

Representative DSC heating curves for the water–gel systems with various types of hydrophobic side chains and with various contents of FMA are shown in Figures 7 and 8, respectively. At temperatures above 0°C, two obvious melting peaks can be observed in the sample LA–AA = 1 and in FMA-modified gels with various contents of FMA, indicating the presence of two states of water (freezing bound water and free water). As a comparison, the DSC curve of unmodified PAA shows only one melting peak at temperatures above 0°C, indicating a small, negligible amount of freezing bound water, which is consistent with the results shown in Table II.

The temperature of the melting peaks for gel–water systems that have similar water content increased in the order LA–AA = 1, FMA–AA = 1, unmodified PAA (shown in Fig. 7). The temperature of the melting peaks for HM gel–water systems was significantly lower than that of the unmodified PAA–gel system. This result suggests that lower energies are needed during the melting process of water for HM gels, which could be ascribed to the higher proportion of nonfreezing water (bound water). The temperature of melting peaks of water in FMA-modified hydrogels decreased with an increasing content of FMA, as can be seen in Figure 8. This shows that the content of nonfreezing water in the gels increased with an increase in the hydrophobic association of FMA. The stronger hydrophobic association improved the formation of the ordered water shell and resulted in increases of n_0. However, it was noticeable that in both HM gels the melting temperature of gel sample FMA–AA = 1 was lower than that of sample LA–AA = 1, although the hydrophobic association of the FMA-modified gel was stronger than that of the LA-modified gel according to the data of swelling. This result is possibly related to the special properties of the fluorocarbon-containing group.

Thermogravimetric analyses

The evaporation temperatures and weight loss of water in the gels measured by thermogravimetric analysis (TGA) are given in Table III. The evaporation temperature of water in HM gels increased by about 10°C–30°C compared to that in the unmodified PAA gel. The water molecules can penetrate inside the unmodified PAA gel more easily, and have much stronger interactions with hydrophilic acrylic acid chains. As the results shown in Table II for the sample FMA–AA = 1 indicate, the melting enthalpy of freezing bound water was higher than that of freezing water, which means the freezing bound water exhibited lower melting and higher freezing temperatures than the freezing water did. Therefore, as shown in Table III, compared with that in the unmodified PAA gel, the higher evaporation temperature of water in the HM gels could be ascribed to the increase of the number (n_1) of freezing bound water in this gel because the hydrophobic association. This conclusion is consistent with the previous results of DSC.

TABLE III
Evaporation Temperature of Water Inside Gels Measured by TGA

	PAA	FMA–AA = 0.2	FMA–AA = 0.5	FMA–AA = 1	FMA–AA = 2	LA–AA = 1
TGA_{max} (°C)	93.67	97.70	109.87	129.52	131.24	125.57
Weight loss (%)	7.985	7.454	6.615	5.215	4.502	8.852

The weight loss of unmodified PAA was greater than that of the sample FMA–AA = 1 (seen in Table III). This phenomenon agrees with the conclusion, derived from the results shown in Table II, that hydrophobic association of hydrophobic side chains in the sample FMA–AA = 1 resulted in an increase in the number (n_0) of bound water (nonfreezing water) molecules.

Atomic force microscopy

Microscopic topography images of gel surfaces were observed by atomic force microscopy (AFM). The AFM images (5×5 μm^2) of the PAA, FMA–AA = 0.5, and FMA–AA = 1 gels are shown in Figure 9. The samples were first immersed in deionized water for 1 week and then were dried in a vacuum oven at 40°C until the desired water contents were obtained. As shown in Figure 9(b), holelike domains with a radius of about 200 nm were observed on the surface region of the sample FMA–AA = 0.5. The formation of holelike domains is related to the aggregation of FMA groups. In hydrophobically modified gels the FMA groups aggregate and form hydrophobic microdomains. Because of poor miscibility between the polymer main chains, consisting of hydrocarbon groups, and the hydrophobic microdomains, consisting of fluorocarbon groups, a phase separation occurred. A similar morphology was observed with the gel sample FMA–AA = 1, except that the holelike domains were larger (with a radius of about 300 nm) and the surface smoother [Fig. 9(c)]. The holelike domains with the even dimension were very regular. This might be ascribed to the increase in the number of hydrophobic microdomains with the increase in FMA. The AFM result shown in Figure 9(a) indicates that the surface image of the unmodified PAA gel was totally different from that of the FMA-modified gels and that no phase separation wa observed in this gel, a sign of the high affinity in the gel without FMA. The results from AFM show that hydrophobic association of FMA took place in the gel networks and thus formed microdomains affecting the water state in gel systems, a result consistent with the previous data from the swelling measurements, TGA, and DSC.

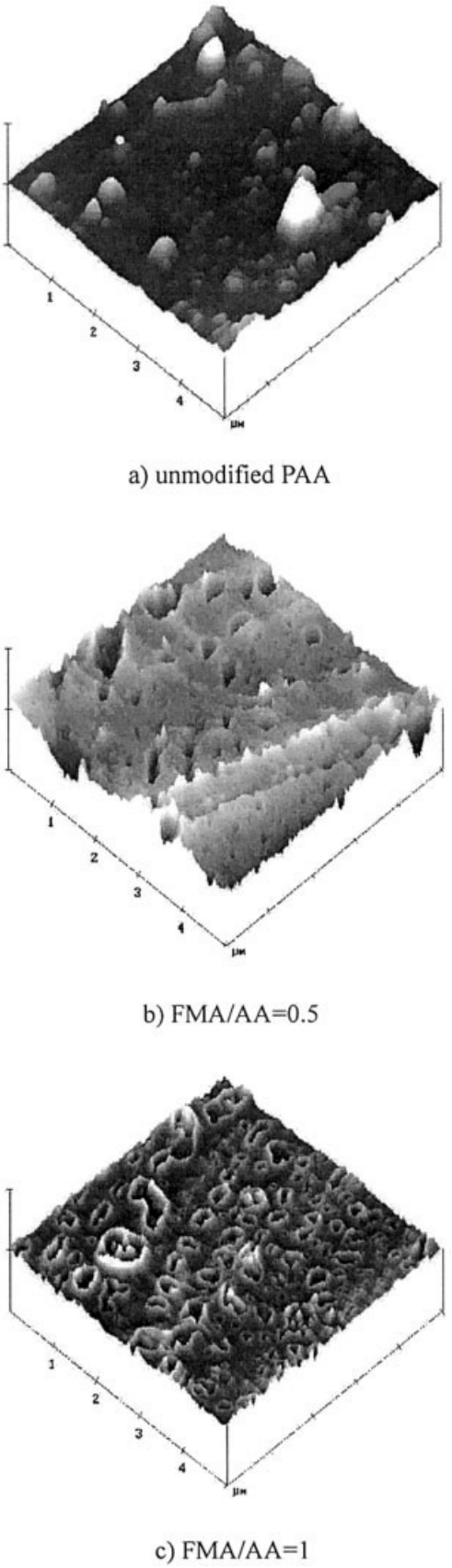


Figure 9 AFM micrographs of gels with different FMA contents.

CONCLUSIONS

The main findings of the present investigation are:

1. A hydrophobic association exists in hydrophobically modified gels, and fluoro-containing FMA groups show a stronger ability for hydrophobic association than LA groups do.
2. The presence of three states of water (free water, nonfreezing water, and freezing bound water) in gels has been proven by the DSC and TGA re-

sults. The melting enthalpies of freezing bound water and free water in the gel sample FMA–AA = 1 were measured as 7589.03 and 6864.06 J/mol, respectively.

3. The numbers of nonfreezing and freezing bound water molecules associated with a polymer unit, n_0 and n_1, increased with the content of FMA and the hydrophobicity of the hydrophobes.
4. The results of AFM showed microscopic phase separation and holelike domains of about 200–300 nm on the surfaces of FMA-modified gels because of the aggregation of FMA groups. The phase separation increased with an increase in FMA content, which was not found in the unmodified gel.

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