

pH-Dependent Swelling Behavior and Network Parameters of Ionic Poly(*N-t*-butylacrylamide-*co*-acrylamide) Hydrogels

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ABSTRACT: Ionic poly(*N-t*-butylacrylamide-*co*-acrylamide) [P(TBA-*co*-AAM)] hydrogels were synthesized by the free-radical crosslinking copolymerization of *N-t*-butylacrylamide and acrylamide monomers in fixed amounts and the maleic acid (MA) comonomer in methanol in different amounts with *N,N*-methylene bis(acrylamide) as the crosslinker, ammonium persulfate as the initiator, and *N,N,N',N'*-tetramethylethylenediamine as the activator. The swelling behavior of these hydrogels was analyzed in buffer solutions at various pHs. The polymer-solvent interaction parameter (χ) and the average molecular weight between crosslinks of the ionic P(TBA-*co*-AAM) hydrogels were calculated from swelling studies in buffer solutions at various pHs and were related to the MA content. The results indicated that the swelling behavior of the ionic P(TBA-*co*-AAM) hydrogels at different pHs agreed with the modified Flory-Rehner equation based

on the affine network model and the ideal Donnan theory. The enthalpy (ΔH) and entropy (ΔS) changes appearing in the χ parameter for the hydrogels were also determined with the modified Flory-Rehner equation. The negative values for ΔH and ΔS indicated that the hydrogels had a negative temperature-sensitive property in water, that is, swelling at a lower temperature and shrinking at a higher temperature. The experimental swelling data of the hydrogels at different temperatures agreed with the modified Flory-Rehner approach based on the affine network model, which ensured that the sensitive dependence of the χ parameter on both the temperature and polymer concentration was taken into account. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1624–1630, 2006

Key words: hydrogels; swelling; transitions

INTRODUCTION

Hydrogel collapse, that is, a drastic reduction of the network volume induced by changes in the external parameters, such as the pH, temperature, solvent composition, and surfactant concentration, has been investigated intensely both experimentally and theoretically.^{1–3} In particular, most dramatic changes in the volume are observed for pH-sensitive hydrogels that contain ionizable groups on polymer chains.^{4,5} The acid or basic pendant groups accept or release protons in response to changes in the environmental pH; when the pendant groups of the hydrogel are changed, electrostatic repulsions are formed, and the sorption of water in the hydrogel is increased. The swelling of hydrogels with acid pendant groups (e.g., carboxylic or sulfonic acid) increases when the pH of the swelling solution is above the pK_a of the ionizable pendant groups. The extent of swelling depends on the number of ionized acidic groups; thus, swelling increases with

the pH of the solution. On the other hand, when the pendant groups are basic (e.g., amines), the swelling of hydrogels increases in solutions whose pH is below the pK_b of the ionizable groups. This fact is usually associated with the presence of freely moving low-molecular-mass counterions, which have to be within the hydrogel because of electroneutrality conditions and generate osmotic pressure within the hydrogel.^{6,7} From a theoretical point of view, this means that the description of the collapse of a pH-sensitive hydrogel must necessarily take into account the translational entropy of the counterions, and analysis shows that the contribution of this term to the total free energy is substantial.⁸ Different polymeric and copolymeric pH-sensitive hydrogels have been synthesized with *N*-vinylimidazole,⁹ *N*-vinyl-2-pyrrolidone,¹⁰ *N*-isopropylacrylamide,¹¹ and acrylamide (AAM)¹² monomers with acrylic acid or itaconic acid as the comonomer. Recently, Özmen and Okay¹³ investigated the swelling behavior of a series of hydrogels based on *N-t*-butylacrylamide (TBA) and AAM monomers of various ratios in solvent mixtures. The swelling ratios of the TBA/AAM hydrogels were influenced strongly by the solvent composition and the change in the molar ratio of the monomers. According to the swelling theories, the equilibrium swelling ratio of hydrogels can

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be achieved by the introduction of charged groups into the network chains.¹⁴

For this purpose, we synthesized strong polyelectrolyte poly(*N*-*t*-butylacrylamide-*co*-acrylamide) [P(TBA-*co*-AAM)] hydrogels with four different maleic acid (MA) concentrations and measured their swelling ratios in buffer solutions at various pHs. The average molecular weight between crosslinks (\bar{M}_c) and the polymer-solvent interaction parameter (χ) of the hydrogels were calculated from equilibrium swelling values. The measured swelling data of the hydrogels were compared with those predicted by the modified Flory-Rehner approach. This simple equation correctly predicted the swelling behavior of the ionic P(TBA-*co*-AAM) hydrogels. Enthalpy and entropy changes appearing in the χ parameter for the P(TBA-*co*-AAM)-water system were also determined.

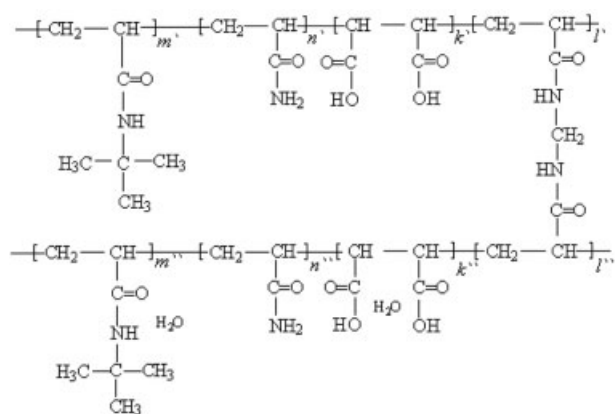
EXPERIMENTAL

Materials

TBA (Aldrich), AAM (Aldrich), MA (Aldrich), *N,N*-methylene bis(acrylamide) (MBAAM; Aldrich), ammonium persulfate (APS; Aldrich), and *N,N,N',N'*-tetramethylethylenediamine (TEMED; Aldrich) were used as received. Glacial CH₃COOH, H₃PO₄ (85%), H₃BO₃, and standardized NaOH were used to prepare Britton-Robinson (B-R) buffers. A B-R buffer solution was prepared in such a way that 2.3 mL of glacial acetic acid, 2.7 mL of phosphoric acid, and 2.47 g of boric acid were dissolved by dilution in triple-distilled water to 1.0 L; 50-mL portions of this solution were taken, and the pH was adjusted between 2.0 and 9.0 by the addition of an appropriate amount of 2.0 M NaOH.

Synthesis of the hydrogels

Hydrogels were prepared by the free-radical cross-linking copolymerization of TBA, AAM, and MA with



Scheme 1 Network structure of ionic P(TBA-*co*-AAM).

TABLE I
Characteristic Parameters Used in the Preparation of the Ionic P(TBA-*co*-AAM) Hydrogels

f_i	$C_0 \times 10^3$ (mol/mL)	\bar{V}_r (mL/mol)
0.0	1.14	82.9
3.7	1.34	83.7
7.1	1.39	84.5
10.3	1.44	86.0
13.3	1.49	108.9
16.1	1.54	108.2

f_i is the mole fraction of MA used in the hydrogel preparation.

a small amount of MBAAM as the crosslinker (see Scheme 1). APS (0.06 M) and TEMED (0.064 M) were used as the redox initiator system. The crosslinker ratio (X ; i.e., the molar ratio of the crosslinker MBAAM to the monomers TBA and AAM) was fixed at 2.7/100, whereas the MA content of the monomer mixture was varied from 3.7 to 16.1 mol %. The synthesis parameters used in the preparation of the hydrogels are presented in Table I. The solutions containing TBA (0.5 g), AAM (0.5 g), MBAAM (0.05 g), APS (2.0 mL), TEMED (2.5 mL), and MA (0.05, 0.10, 0.15, 0.20, and 0.25 g) were prepared in 4.0 mL of methanol with various compositions [TBA + AAM/MA molar ratio = 96.3/3.7, 92.9/7.1, 89.7/10.3, 86.7/13.3, or 83.9/16.1]. After nitrogen bubbling for 15 min, these solutions were placed in poly(vinyl chloride) straws 4 mm in diameter and about 20 cm long. The poly(vinyl chloride) straws were sealed and immersed in a thermostated water bath at 20°C, and the polymerization was conducted for 24 h. After the reaction, the hydrogels were cut into specimens approximately 10 mm long, dried in a vacuum oven at 50°C to a constant weight, and subjected to Soxhlet extraction with water to remove the uncrosslinked polymer and unreacted MA from the copolymers. The extracted gels were dried again in a vacuum oven at 50°C to a constant weight. When the aqueous extract was titrated with NaOH (0.05M), end-point detection was not observed because there was no unreacted MA. The volume fraction of the polymer network after preparation (ν_{2r}) was calculated as follows:

$$\nu_{2r} = \left[\frac{1 + \left(\frac{m_r}{m_d} - 1 \right) \rho_2}{\rho_1} \right]^{-1} \quad (1)$$

where m_r and m_d are the masses of the hydrogel after the preparation and after drying and ρ_2 and ρ_1 are the densities of the polymer network and solvent, respectively. The ρ_2 and ρ_1 values were 1.10 and 1 g/mL, respectively. The density of the polymer network was determined by a pycnometer with acetone as a non-

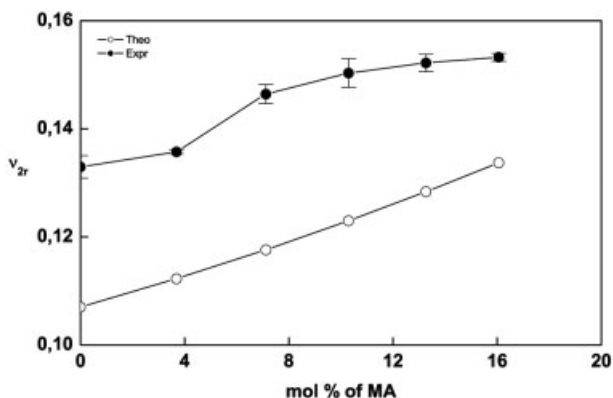


Figure 1 Variation of ν_{2r} with the molar percentage of MA. The experimentally and theoretically determined ν_{2r} values are indicated.

solvent. The density value of the P(TBA-co-AAm) copolymeric networks did not change so much with the MA content. On the other hand, ν_{2r} could also be calculated from the initial monomer concentration (C_0 ; mol/mL) as follows:¹⁵

$$\nu_{2r} = C_0 \bar{V}_r \quad (2)$$

where \bar{V}_r is the average molar volume of the polymer repeat units. \bar{V}_r can be calculated as follows:

$$\bar{V}_r = \frac{M_{n1}f_{n1} + M_{n2}f_{n2} + M_i f_i}{\rho_2} \quad (3)$$

where M_{n1} is the molecular mass of the first neutral unit, f_{n1} is the molar fraction of the first neutral unit, M_{n2} is the molecular mass of the second neutral unit, f_{n2} is the molar fraction of the second neutral unit, and M_i is the molecular mass of the ionic units in the gel system.

The theoretical values of ν_{2r} , calculated with eq. (2), are shown in Figure 1 as open symbols together with the experimentally determined ν_{2r} values (filled symbols). The experimental ν_{2r} values are larger than the theoretical ones because of the presence of bound water in the hydrogel. Hence, the theoretical ν_{2r} values were used for further calculations.

Measurement of the equilibrium swelling ratio

To measure the swelling ratio, preweighed dry samples were immersed in the pH solutions. After the excess water was wiped off the sample surface with moistened filter paper, the mass of the swollen samples was measured in the pH range of 2–9.

The equilibrium swelling ratio of the hydrogels (q_v) was determined as follows:

$$q_v = \frac{1 + \left(\frac{m_s}{m_d} - 1\right)}{\rho_1} \quad (4)$$

where m_s is the mass of the hydrogel after equilibrium swelling in the pH solution. The volume fraction of the polymer network (ν_{2m}) was calculated as follows:

$$\nu_{2m} = 1/q_v \quad (5)$$

Measurement of the swelling kinetics

For the swelling dynamic studies, the hydrogels were immersed in pH 2, 5, or 9 solutions. At a prescribed time interval, the hydrogels were taken out from the water and weighed after excess water was wiped off the surface of the hydrogels. The swelling ratio (SR) of the hydrogels was defined as follows:

$$SR = \frac{m_t - m_d}{m_d} \quad (6)$$

where m_t is the mass of the wet hydrogel at each time.

All the reported swelling values are averages of at least three separate measurements.

RESULTS AND DISCUSSION

pH-dependent swelling behavior

Polyelectrolyte hydrogels usually exhibit different degrees of equilibrium swelling at different pH values depending on the ionic composition and polymeric molecular structure. According to the acid–base equilibrium for a weak acid, in an acidic solution, most of the acidic units remain in the protonated form and ionize under basic conditions. In this respect, the equilibrium swelling ratios of the ionic P(TBA-co-AAm) hydrogels have been measured in different pH solutions and are presented in Figure 2. The equilibrium swelling ratio of the hydrogels takes place in a step-wise manner because of a large difference in the pK_a values (nominal $pK_{a1} = 1.83$ and $pK_{a2} = 6.07$). The swelling shows sudden increases at the pH values around the corresponding pK_a values. In addition, the equilibrium swelling ratios of these hydrogels are smallest in low-pH solutions because of the presence of strong hydrogen bonds between the carboxylic acid groups. Above the pK_a values of MA ($pH > 6$), the carboxylic acid groups transform into the ionized form (COO^-) as the pH value of the buffer solution increases. The electrostatic repulsion between the ionized groups causes the hydrogels to swell.¹⁶ On the other hand, the value of the equilibrium swelling ratio of an ionic hydrogel very much also depends on the number of ionizable groups in the hydrogel. An in-

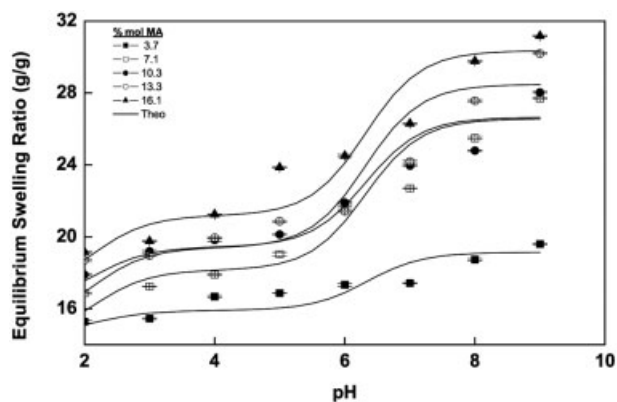


Figure 2 Changes in the equilibrium swelling ratios with pH for the ionic P(TBA-co-AAm) hydrogels. The experimental data are shown as symbols. The solid lines were calculated with eq. (7).

crease in MA produces an equilibrium swelling ratio, which increases dramatically at all pH values, especially for hydrogels with 3.7 and 7.1 mol % MA, for which the number of ionic units is relatively high. Also notable is the fact that the addition of only a minute amount of MA (3.4 mol %) radically changes the swelling behavior of these hydrogels. This is due to the fact that as the MA content in the P(TBA-co-AAm) hydrogel increases, the charges on the polymeric chains also increase. As a result, this leads to the expansion of the hydrogels because of the high electrostatic repulsion, so the swelling capacities of the hydrogels increase.

The swelling ratio as a function of time for the ionic P(TBA-co-AAm) hydrogels in several pH buffer solutions is shown in Figure 3. As usual, the swelling ratios of these hydrogels increase at short times and level off to maxima at longer times. The results show that under acidic conditions (pHs 2 and 5), most carboxylic acid groups in MA are in the form of $-\text{COOH}$, and the hydrogel collapses. At high pH values (pH 9), the number of carboxylate ions in the hydrogel increase, and the resulting electrostatic repulsion in the polymer network causes the hydrogel to swell. The maximum swelling ratio occurs at pH 9, indicating the complete neutralization of carboxylic acid groups. This is the general trend in ionizable hydrogels.

Network parameters

The equilibrium swelling ratio of ionic hydrogels is known to depend on \overline{M}_c , χ , and the charge densities of the network as well as the polymer network concentration after the hydrogel preparation. These factors are related to the concentration of the crosslinker, the ionic comonomer, and the total concentration of the monomers in the initial reaction mixture. The Flory–Rehner theory, including the ideal Donnan equilibria,

gives the relationship between the equilibrium swelling ratio of hydrogels in water and the three synthesis parameters.¹⁷ By considering Flory and Rehner's pioneering work, including the ideal Donnan equilibria, we obtained a modified expression from which \overline{M}_cM and χ could be determined simultaneously for an ionic hydrogel with diprotic acid:³

$$\left[\frac{2K_{a1}K_{a2} + 10^{-\text{pH}}K_{a1}}{2[(10^{-\text{pH}})^2 + 10^{-\text{pH}}K_{a1} + K_{a1}K_{a2}]} \right] \frac{V_1 f_i^2 v_{2m}^2}{4IV_r^2} = \ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2 + F \frac{V_1 \rho_2 v_{2r}^{2/3} v_{2m}^{1/3}}{\overline{M}_c} \quad (7)$$

In this equation, the relevant experimental parameters for the ionic P(TBA-co-AAm) hydrogels are as follows: the first and second dissociation constants of MA ($K_{a1} = 1.48 \times 10^{-2}$ and $K_{a2} = 8.51 \times 10^{-7}$), the molar volume of the solvent ($V_1 = 18 \text{ mL/mol}$), the ionic strength of the swelling medium ($I = 1.0 \times 10^{-4} \text{ mol/mL}$), and the front factor for the affine network ($F = 1$). Details about eq. (7) have been reported elsewhere.³

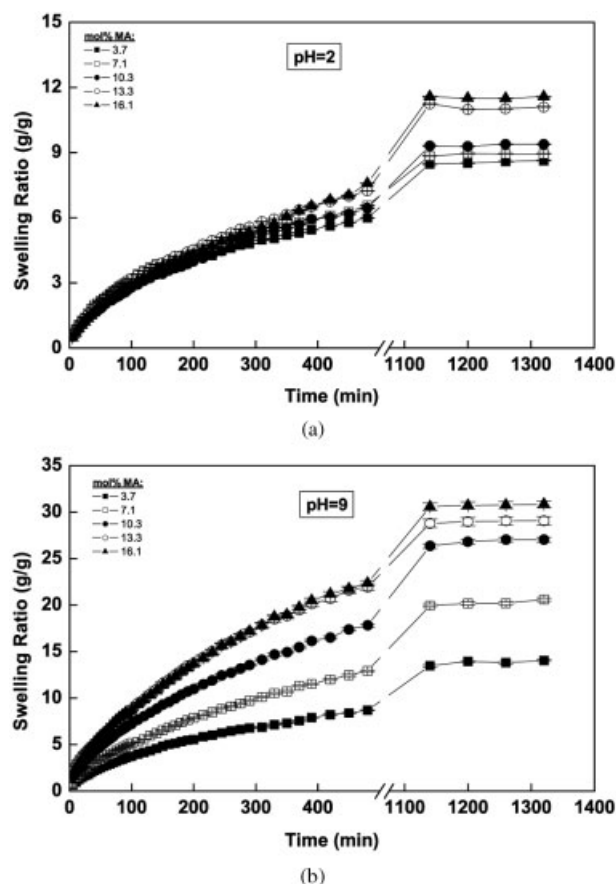


Figure 3 Swelling ratio as a function of time for the ionic P(TBA-co-AAm) hydrogels at 25°C at different pHs (the pH values of the buffer solutions are shown).

TABLE II
 χ and \overline{M}_C Values of the Ionic P(TBA-co-AAm) Hydrogels

MA (mol %)	χ	$\overline{M}_C(\text{expr})$ (g/mol)	$\overline{M}_C(\text{chem})$ (g/mol)
3.7	0.483 ± 0.004	24,000	1,350
7.1	0.480 ± 0.005	21,000	1,400
10.3	0.443 ± 0.013	9,300	1,500
13.3	0.434 ± 0.019	7,500	1,550
16.1	0.393 ± 0.026	5,700	1,600

The change in the equilibrium swelling ratio of the ionic P(TBA-co-AAm) hydrogels in pH buffer solutions was used to evaluate \overline{M}_C and χ . For this purpose, by the expansion of the logarithmic series, eq. (7) was rearranged for the determination of \overline{M}_C and χ , and eq. (8) was obtained:

$$\left[\frac{2K_{a1}K_{a2} + 10^{-pH}K_{a1}}{2[(10^{-pH})^2 + 10^{-pH}K_{a1} + K_{a1}K_{a2}]} \right]^2 \frac{V_{f_i}^2}{4IV_r^2} 0.5 = \chi + F \frac{V_1 \rho_2 v_{2r}^{2/3} v_{2m}^{-5/3}}{\overline{M}_C} \quad (8)$$

With the experimentally measured polymer volume fraction (v_{2m}) of the gels in their equilibrium-swollen state and the aforementioned data, a plot of the left-hand side of eq. (8) versus $FV_1 \rho_2 v_{2r}^{2/3} v_{2m}^{-5/3}$ gives a straight line, with $1/\overline{M}_C$ and χ as the slope and intercept of the horizontal axis, respectively. The \overline{M}_C and χ values determined via linear regression analysis are listed in Table II.

The \overline{M}_C values of the hydrogels decrease from 24,000 to 5700 g/mol with increasing MA content. This behavior can be interpreted as MA being effective in the crosslinking process. In addition, the reduction of the \overline{M}_C values with increasing MA content can be connected to the condensation of counterions to ion pairs.^{15,18} Ion pairs attract each other because of dipole-dipole interactions and thus act as physical crosslinks in the hydrogel.

On the other hand, $\overline{M}_C(\text{chem})$, which results if all the crosslinker molecules form effective crosslinks in the hydrogel, can be calculated from the X value used in the hydrogel synthesis with the following equation:¹⁵

$$\overline{M}_C(\text{chem}) = \frac{\overline{V}_r \rho_2}{2X} \quad (9)$$

Although X was fixed at 2.7/100 for the hydrogel preparation process, $\overline{M}_C(\text{chem})$ slightly increased with increasing MA content because of the larger molar volume of MA compared with that of the TBA and AAm units. The experimentally found \overline{M}_C values of

the hydrogel with 3.7 mol % MA are 18 times higher than the theoretically calculated counterpart. This value decreases to 6.2 and 3.6 when 10.3 and 16.1 mol % MA is used in the hydrogel preparation, respectively. The difference between the chemical and experimental \overline{M}_C values of the hydrogels indicates that a significant fraction of the crosslinker MBAAm is wasted during the crosslinking copolymerization, probably because of the cyclization and multiple crosslinking reactions. The high degree of dilution during the hydrogel preparation as well as the higher crosslinker reactivity is mainly responsible for this reaction.¹³

However, the χ parameter of the hydrogels is slightly decreased by the incorporation of MA into the polymer chain. It is known that this parameter depends on the temperature and, for many systems, also on the composition. The use of eq. (8) for calculating the parameter neglects both the composition and temperature dependence. In this case, one possible explanation for the variation of χ with the MA content is related to the change in the chemical structure of the network chains, which can alter the value of the χ parameter.

On the other hand, to control the modified Flory-Rehner equation and validity of \overline{M}_C and χ of the ionic P(TBA-co-AAm) hydrogels, the theoretical swelling ratios depending on pH were calculated with eq. (8). The solid curves in Figure 2 represent the theoretical swelling ratio of the hydrogels as a function of pH. The prediction of the modified Flory-Rehner equation based on the affine network model and the ideal Donnan theory agrees reasonably well with the experimental swelling data of the hydrogels in buffer solutions at various pHs. We can thus conclude that the modified Flory-Rehner equation based on the affine network model and the ideal Donnan theory can be used to predict the swelling behavior of ionic hydrogels in buffer solutions at various pHs.

Effect of the temperature on the swelling equilibrium

Figure 4 illustrates the temperature dependence of the equilibrium swelling ratio of the ionic P(TBA-co-AAm) hydrogels with different MA contents in water when the temperature increases from 5 to 60°C.

The incorporation of MA into a crosslinked hydrogel affects the swelling behavior of the hydrogel in two opposite directions. The introduction of MA can dramatically increase the equilibrium swelling ratio below the volume-phase-transition temperature, but the phase transition shifts to higher temperatures and the volume collapses within a broad temperature range. As shown in Figure 4, the temperature intervals for the volume-phase transition are 10–15 and 10–30°C for the hydrogels with 3.7 and 16.1 mol % MA,

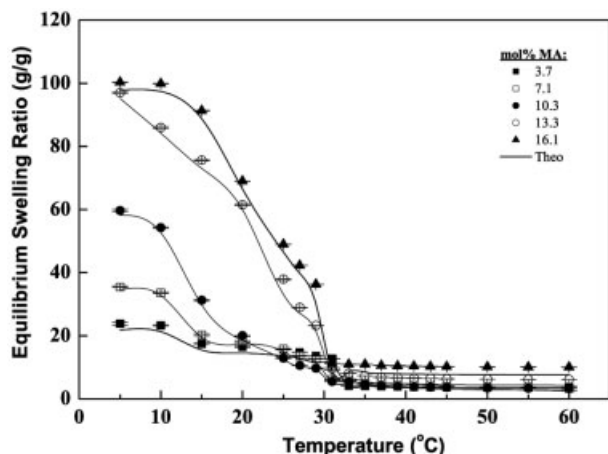


Figure 4 Variation of the equilibrium swelling ratio of the ionic P(TBA-co-AAm) hydrogels with different MA contents as a function of the temperature in water. The experimental data are shown as symbols. The solid curves were calculated with eqs. (7) and (12).

respectively. Thus, as the ionic group content is increased, the temperature interval at the volume-phase transition becomes broader. This result contradicts the prediction of the theories because the osmotic pressure of the counterions should induce a discontinuous volume change in an ionic hydrogel. These unusual properties can be explained by the heterogeneity of the molecular-level chemical composition of the polymer chains.¹³ In this case, TBA and AAm segments may be distributed along the network chains heterogeneously because of the different solubilities of the monomers.¹³ The chains of the hydrogels with low MA contents may undergo the volume-phase transition earlier, that is, at lower temperatures, than the other chains. As a result, it is apparent that the equilibrium swelling ratio and the volume-phase transi-

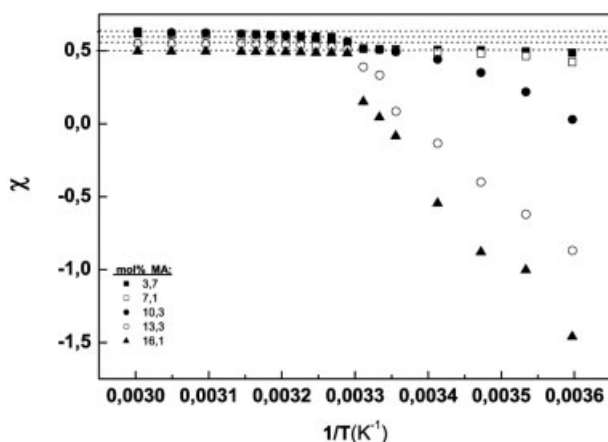


Figure 5 Variation of the χ parameter for the ionic P(TBA-co-AAm)-water system as a function of the inverse temperature. The molar percentage of MA is indicated.

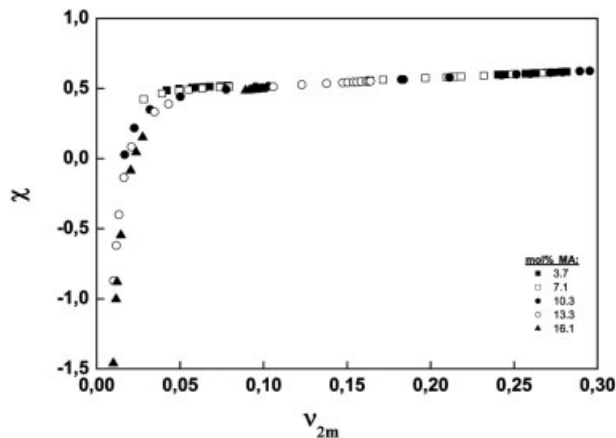


Figure 6 Variation of the χ parameter for the ionic P(TBA-co-AAm)-water system as a function of v_{2m} . The molar percentage of MA is indicated.

tion of the ionic P(TBA-co-AAm) hydrogels can be controlled by the incorporation of more hydrophilic units such as MA into the hydrogel system.

χ

One of the basic structural parameters of crosslinked polymeric networks is χ . It is well known that this parameter depends on the temperature and, for many systems, also on the composition. The χ parameter is expressed as a series expansion in powers of v_{2m} :¹⁹

$$\chi = \chi_1 + \chi_2 v_{2m} + \chi_3 v_{2m}^2 + \dots \quad (10)$$

where coefficients χ_1 , χ_2 , and χ_3 are the functions of the temperature and the molecular characteristics of the polymer-solvent system. For a high swelling ratio, the v_{2m} dependence of χ can be neglected as defined by eq. (11). In this case, χ reduces to χ_1 , and the following equation can be obtained for it:¹⁷

$$\chi_1 = \frac{\Delta H - T\Delta S}{RT} \quad (11)$$

where ΔH and ΔS are the changes in the enthalpy and entropy, R is the gas constant, and T is the tempera-

TABLE III
 ΔH and ΔS for the χ Parameter for the Ionic P(TBA-co-AAm) Hydrogels

MA (mol %)	ΔH (J/mol)	ΔS (J/mol)
3.7	-295.3	-12.7
7.1	-397.3	-14.3
10.3	-897.3	-28.6
13.3	-2514.2	-70.6
16.1	-3482.5	-95.5

TABLE IV
Coefficients for the Dependence of χ on the ν_{2m} and Temperature Values

MA (mol %)	χ_1	a	b	c	d
3.7	0.485	0.420	0.099	0.203	0.100
7.1	0.474	0.506	0.098	0.031	0.100
10.3	0.477	0.431	0.099	0.238	0.100
13.3	0.468	0.266	0.026	0.470	0.121
16.1	0.438	0.244	0.070	0.447	0.099

ture, respectively, during the swelling of the crosslinked polymer in a solvent. With eq. (7), the χ parameters at each temperature were calculated from ν_{2m} values. The variation of the χ parameter with $1/T$ and ν_{2m} for the ionic P(TBA-co-AAm) hydrogels are given in Figures 5 and 6. As shown in Figure 5, at high temperatures, that is, at low swelling ratios, χ is almost independent of the temperature changes. This indicates that the enthalpy and entropy contributions to the χ parameter are constant. In this case, χ equals χ_1 at this swelling ratio and temperature range.¹⁷ The dashed lines in Figure 5 are the linear regression lines obtained from the high-temperature range of the data points.

ΔH and ΔS values appearing in the χ_1 parameter were determined from the slopes and intercepts of these lines. ΔH and ΔS values of the hydrogels are given in Table III. The signs of both quantities are negative for all the hydrogels. The negative values for ΔH and ΔS indicate that the ionic P(TBA-co-AAm) hydrogels have lower critical solution temperatures in water.²⁰ In addition, the absolute values of both ΔH and ΔS increase with an increasing amount of MA, and this indicates that the temperature sensitivity of the hydrogels increases with increasing MA content.

Nonlinear regression analyses of the data (χ , ν_{2m} , and T) for all the P(TBA-co-AAm) hydrogels gave the following relationship for the dependence of χ on ν_{2m} and T :²⁰

$$\chi = \chi_1 + \left(a - \frac{b}{T}\right)\nu_{2m} + \left(c - \frac{d}{T}\right)\nu_{2m}^2 \quad (12)$$

The coefficients for each hydrogel are given in Table IV. The theoretical equilibrium swelling ratios of the hydrogels calculated with eqs. (7) and (12) are shown

in Figure 4 as a solid curve plotted as a function of the temperature. For comparison, the experimental data points are also given in the figure as symbols. After we take into account the sensitive dependence of the χ parameter on both ν_{2m} and T , the prediction of the modified Flory–Rehner approach provides satisfactory agreement with the experimental swelling data.

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