Water–polymer interactions and critical phenomena of swelling in inhomogeneous poly(acrylonitrile–acrylamide–acrylic acid) gels

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The water uptake and swelling behaviour of physically crosslinked, inhomogeneous poly(acrylonitrile–acrylamide–acrylic acid) hydrogels from 10 to 60°C were determined by gravimetry/differential scanning calorimetry and volume measurement, respectively. The contents of water and its non-bound portion were found to reach a minimum value at acrylamide content around 33.5 mol%, at which the water uptake of this gel does not vary with the temperature. The non-bound water was found to decrease gradually and then increase with increasing amide concentration. The duration of the post-gelation treatment between -10 and 10°C was also shown to be one of the factors affecting the extent of the water uptake in gels. The critical endpoint temperatures (T_cs) of hydrogels, obtained from volume phase transition data upon changing the acetone concentration in aqueous solutions at various temperatures, were shown to decrease with the increasing acid or amide contents. The water uptake for gels with lower amide contents decreases with increasing temperature. However, there is an opposite trend for water uptake in gels with higher amide content, and the critical points on the plots of the amount of water uptake *versus* temperature appear at a temperature equal to T_c.

(Keywords: inhomogeneous hydrogels; swelling; phase transition)

INTRODUCTION

Hydrogels are mixtures that consist of a substantial amount of water and highly swollen, hydrophilic polymer networks. Notably, the water-absorption characteristics of gels are among the major factors affecting the diffusive behaviour of small molecules through gels, interfacial energetics of gels, volumetric property of temperature-sensitive gels, and so on.

With regard to the state of water in gels, Lee *et al.*[1] used calorimetric data for water freezing to assign three states of water, in which the bound water was associated with the polymer and the non-bound water, made up of free and intermediate parts, had a lower interaction energy with the polymer network. McBrierty and co-workers[2,3] used ^{1}H nuclear magnetic resonance to find that the bound water in gels did not exist in the crystalline form of ice at temperatures lower than 0°C and that this amorphous water had a glass transition temperature of -90°C. Pedley and Tighe[4] studied the three states of water in styrene/2-hydroxyethyl methacrylate (HEMA) copolymers over a rather wide range of monomer compositions and concluded that the HEMA segments in excess amount were clustered and phase-separated from the hydrophobic component to result in a minimum on the plot of water uptake against HEMA concentration. The above studies on the abundance of the three water states are concerned with non-ionic hydrogels and there appears to be no report dealing with polyelectrolyte gels.

The physical behaviour of the swollen state of hydrogels is mainly affected by the thermodynamic interactions of polymer–solvent pairs. Tanaka and co-workers[5,6] utilized the Flory–Huggins theory to derive the osmotic pressure of gels by taking into account the polymer–polymer affinity in solution, rubber elasticity, and hydrogen ion pressure caused by ionizable groups on polymer chains. Since the osmotic pressure of polyelectrolyte gels is dependent on the environmental conditions such as temperature, solvent composition, pH, etc., the change in the above variables from one state to another causes volume phase transition, which might find applications in artificial muscles, chemical actuators and regulated drug delivery devices.

Tanaka[7] further investigated the polyacrylamide gels and visualized the aforementioned discontinuous volume change as analogous to the two-phase coexistence region in the phase diagram for the pure substance. The critical point in the phase diagram for small molecules is also equivalent to the critical endpoint on the plot of gel volume against the thermodynamic variables. Dong and Hoffman[9] explained the volume shrinkage (deswelling) caused by the temperature rise in the poly(*N*-isopropylacrylamide) gels as the transition from the single phase

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to the immiscible two phases through the lower critical solution temperature defined in the solution theory.

The crosslink density or the concentration of crosslinkers was found to cause the water absorption and mechanical strength of polyacrylamide gels to exhibit a minimum and a maximum, respectively, at a certain crosslinker concentration. Under such a condition, the hydrating ability of polymer is minimal, approaching the Θ-condition which defines the 'ideal gel'[9]. Although the osmotic data for such a system were reported in ref. 9, the energetics of the ideal gel have not, to the best of our knowledge, been investigated.

Poly(vinyl alcohol) (PVA) hydrogels have been extensively studied regarding the effect of cyclic freezing–thawing on pregelation and paracrystalline structure[10], as well as chain entanglement and elastic modulus[11]. It was found that the number of thermal cycles enhances the crosslinked structure and the amount of bound water in the light of the three-state-water model[12]. Peppas and Stauffer[13] proposed that the freezing–thawing treatment led to the formation of microgels and crystallites, as well as structural densification due to partial phase separation. However, the effect of freezing–thawing on the structure/thermodynamics of multicomponent, multiphase hydrogels remains open to further study.

After a perusal of published literature, it may be realized that the water–polymer interactions in multicomponent inhomogeneous gels and their dependence on the freezing–thawing conditions deserve further work. Nevertheless, to understand the influence of more complex gel structure on the critical phenomena or phase transition of gels provides the validation for Tanaka's theory. Their paper is aimed at investigating the mode(s) of hydration and interaction energetics of physically crosslinked poly(acrylonitrile–acrylamide–acrylic acid), (P(AN–AAm–AA)), hydrogels, as affected by the chemical composition of polymers, temperature, and freezing–thawing treatment. Furthermore, the critical phenomenon of gel swelling as a function of temperature and composition of surrounding solutions is studied, and the critical temperatures of gel samples are thereafter incorporated into the temperature dependence of gel swelling.

EXPERIMENTAL

Preparation of P(AN–AAm–AA) gels

Acid hydrolysis of PAN. Xerogels, water-free gels, were first prepared through the hydrolysis of polyacrylonitrile (Aldrich, number-average molecular weight (M_n) = 80 000) with concentrated (62 wt%) nitric acid at various reaction times from 8 to 22 h, and subsequently placed at −10°C for 7 days. The preparation procedure was also reported previously[14]. The products were then neutralized with a 1 wt% solution of sodium bicarbonate, until the pH reached 7. The neutralized solution was then dried in a vacuum oven at 70°C.

Quantitative analysis of chemical compositions. The dried polymer obtained in the previous section was dissolved into dimethyl sulfoxide (DMSO), and the mole percentage of amide groups to total functional groups, including nitriles, carboxyls and amides, was analysed with a ^{1}H NMR (Bruker AC-200). The area of the amide resonance peak at a chemical shift (δ) equal to 6.7 to 6.8 ppm and that of the methylene peak at $\delta = 2.0$ ppm was used to calculate the mol% of amide:

$$\text{mol\% of amide} = [\tfrac{1}{2}\text{ peak area for amide})/(\tfrac{1}{2}\text{ peak area for methylene})] \times 100 \qquad (1)$$

The content of acrylic acid was determined by the titration of polymer/DMSO solutions with 0.0842 M aqueous KOH solution in accord with the following approximate relationship:

$$\text{mol\% of carboxyl} = [(\text{volume of KOH solution}) \times (\text{molality of KOH solution})/(\text{weight of polymer in solutions})/(71A + 53(1\text{-}A)] \times 100 \qquad (2)$$

where A = mol% of amide given by equation (1) divided by 100.

Gelation and freezing–thawing treatment. The dried polymer samples were dissolved in DMSO at 70°C, and then mixed with water. The final concentration was 1 g of polymer in 13 ml DMSO and 3 ml water. The solutions were then cooled down to room temperature, placed at −10°C for 12 h (freezing cycle), and then at 10°C for 12 h (thawing cycle). These two steps were repeated one, three or seven times in this study. Samples were finally washed and soaked with deionized water.

Determination of swelling

Volume phase transition. The water-swollen gels (thickness, 5 mm and diameter, 10 mm) were equilibrated with acetone/water solutions (wt% of acetone = 20–80) for 5 days. It should be mentioned that all gel samples in acetone/water solutions had constant dimensions at 3 days, indicating equilibrium swelling after that. The swelling ratio (defined as V^*/V, where V^* = equilibrium volume of gel swollen in pure water at 30°C, and V = equilibrium volume of gel swollen in acetone/water solutions at 30°C) was plotted against the weight concentration of acetone in solutions. The temperatures of the solution baths were varied between 2 and 60°C.

Swelling versus *temperature.* In the deionized water, the swelling ratios as defined above and the water absorption (the ratio of the weight of water absorbed to that of hydrogel) at 5 days were examined as functions of temperature ranging from 10 to 90°C.

Amount of water from differential scanning calorimetry (d.s.c.)

The gel samples were mounted in tightly sealed sample pans which prevented vapour leakage up to 5 atm (~5×10^5 Pa). A calorimeter (DuPont 2000 with data analyser) under nitrogen environment was used. Samples were cooled from room temperature down to −60°C, and then heated to 40°C at a heating rate of 5°C min^{-1}. The content of bound water is the limiting value of the water content in a gel at zero enthalpy of fusion of the gel[1]. This extrapolated value was taken from the plot of the d.s.c. enthalpy of fusion of gel *versus* the non-equilibrated water content in the gel which did not reach equilibrium absorption with the water bath.

RESULTS AND DISCUSSION

Chemical compositions of gels

The chemical compositions of copolymer gels analysed by ^{1}H n.m.r. and base titration are listed in *Table 1*. It

Table 1 Compositions of acrylamide (AAm) and acrylic acid (AA) of the gels with various times of hydrolysis of polyacrylonitrile

	Sample code							
	TPH8	TPH10	TPH12	TPH13	TPH14	TPH16	TPH18	TPH20
Hydrolysis time (h)	8	10	12	13	14	16	18	20
AAm (mol%)	13.22	22.00	30.90	33.50	35.00	36.79	38.80	39.70
AA (mol%)	0.50	0.60	0.78	0.90	1.00	1.20	1.50	2.21

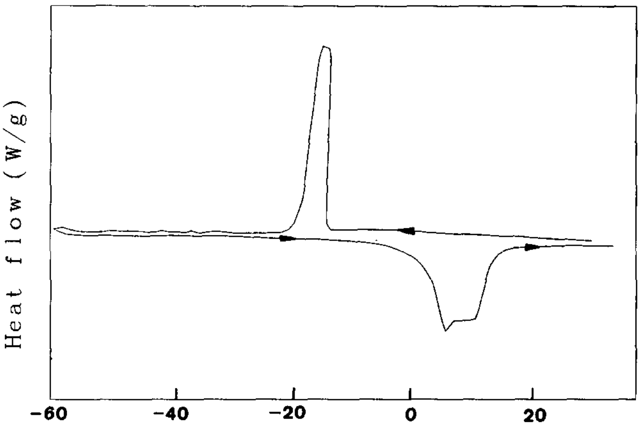

Figure 1 D.s.c. thermograms for TPH8 (freezing–thawing time = 3 days), with cooling run and subsequent heating at a rate of 5°C min^{-1}. The upward-pointing peak represents the exothermic process

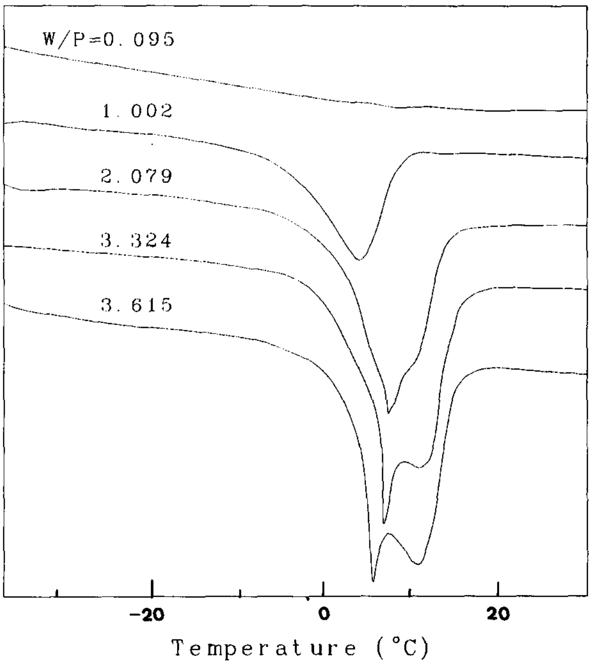

Figure 2 D.s.c. thermograms for TPH8 (freezing–thawing time = 3 days) with various unsaturated water uptake at 30°C. *W/P*, weight ratio of water absorbed to dried polymer

is seen that the amide and acid contents of all samples increase with the duration of acid hydrolysis. The mole percentage of acrylamide in the copolymers ranges from 13.22 to 39.7, and acrylic acid from 0.5 to 2.21. The remaining component in the gels is acrylonitrile.

Modes of unbound-water uptake

A d.s.c. thermogram is shown in *Figure 1*, for water-saturated sample TPH8 (hydrolysis time, 8 h and freezing time, 3 days) going through the heating and cooling steps. An exotherm appears at −19°C while being cooled from room temperature to −60°C. This peak is caused by the freezing of supercooled water, which is located in the restricted space in the pores of gels[3,15]. The d.s.c. endotherms around the fusion points of water for the TPH8 gel with various unsaturated water uptakes (ratio of weight of water to dry polymer = 0.095 to 3.615) are shown in *Figure 2*. As the water uptake increases, the splitting of the melting peak becomes more apparent. It is already known that the intermediate water in the non-bound part exhibits lower melting temperatures than the free water, as stated in the three-state-water model[1]. Therefore, *Figure 2* implies that the free water portion becomes more distinct thermodynamically as the hydrogels gradually approach the equilibrium state with bulk water. For the relatively smaller amount of unsaturated water in gels ($W/P < 2.079$), there seems calorimetrically to be only one phase in the unbound water portion. As the water absorption exceeds a certain value, the two phases become distinguishable. The peak at lower temperature is due to the appearance of the more ordered intermediate water, and the peak at approximately 11°C to the free water. The fusion points of the two kinds of unbound water are greater than that for the free bulk water, which is not restricted to the voids in the gels. This superheating phenomenon may be caused by specific interactions among functional groups (i.e. amides and carboxyls) in polymers with water. Both water supercooling and ice superheating may be caused by the porous structure of gels and chemical interactions between water and functional groups.

Figure 3 shows thermograms for six water-equilibrated gels, and the melting peaks for intermediate water (at ~5°C) and free water (at ~10°C), respectively. At the lowest amide level, a sharp peak for fusion of intermediate water is identified. However, the intermediate water becomes indistinguishable when the mole percentage is greater than 38.8. This also indicates that the free water portion becomes more distinct thermodynamically as the contents of amides or acids in gels progressively increase. It should be mentioned that PHEMA, with less water uptake than any gel in this study, has a more recognizable zone for intermediate water on d.s.c. thermograms[1].

By combination of *Figures 2* and *3*, it may be visualized that the water penetrates into the polymer to fill first the binding sites, until the sites are fully occupied, then the intermediate zone, and finally the free state with the least ordering. The literature reported the fusion points for intermediate and free water in PHEMA hydrogels to be below 0°C[1]. The difference of fusion points between P(AN–AAm–AA) and PHEMA gels may be attributed to the stronger chemical interactions between polymer and

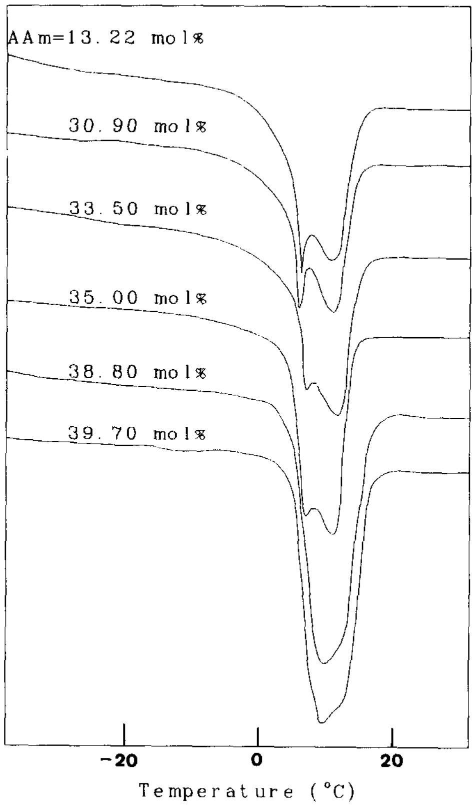

Figure 3 D.s.c. thermograms for hydrogels with various acrylamide contents, at 30°C and in equilibrium with water. AAm, mole percentage of acrylamide

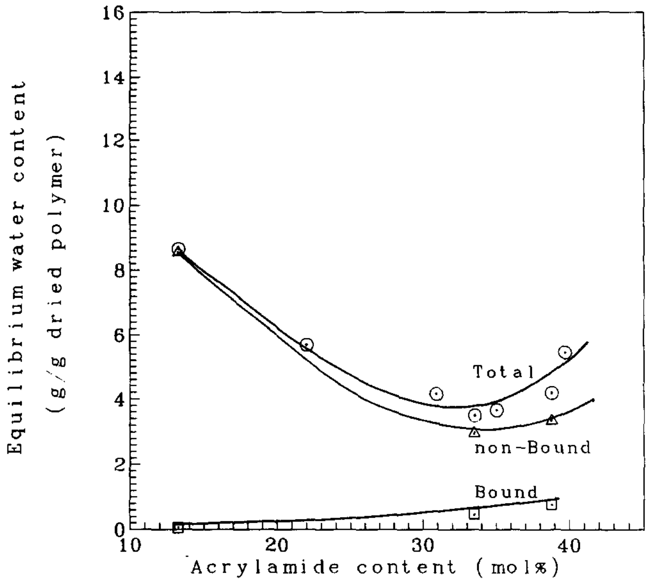

Figure 4 Composition dependence of amount of water in various states and water in total. All samples were treated with a 1-day freezing–thawing process

water in the former. This point can be partly supported by the higher water absorption by P(AN–AAm–AA) than PHEMA.

Effects of chemical composition and freezing–thawing on water uptake

The total water absorption and content of bound water in gels, using gravimetric and d.s.c./extrapolation methods, respectively, are depicted in *Figure 4* as a function of acrylamide content of gels with one cycle of freezing and thawing. The amount of bound water per unit mass of dry polymer increases monotonically with the relative abundance of amides in xerogels. However, the amount of non-bound water shows some complexity in *Figure 4*. The amount of non-bound water is a decreasing function at amide contents from 13 to 33 mol%. This might be due to the fact that more amides cause a more inhomogeneous structure or clusters, and hence a more significant densification of structure which leads to the lower water absorption[4]. Inhomogeneous crosslinked networks were shown through the small-angle X-ray scattering technique to be made up of two regions. One is the homogeneous, density-fluctuating and liquid-like regime. The other possesses the higher crosslink density with solid-like characteristics[9]. At amide content equal to 33.5 mol%, the spatially averaged crosslink density or densification of gels reaches a maximum. As long as the mole percentage of AAm is greater than 33.5, the increasing acrylic acids result in more network defects or transition layer between the immiscible acrylonitrile-rich phase and the AAm-rich one. The more network defects or interphase zone, the more water the gels can accommodate. This minimum water uptake phenomenon as affected by the chemical composition has been observed for systems of interpenetrating polymer networks[16].

Figure 4 shows an interesting feature, namely that the non-bound water portion in P(AN–AAm–AA) gels contributes most, say 80–90 wt%, to the total water uptake. For comparison purposes, this value range is much higher than the value of 40 wt% for PHEMA[17].

Figure 5 shows the weight of bound, non-bound and total water *versus* amide content for gels with 3-day, or three cycles of, freezing and thawing. By combination of *Figures 4* and *5*, it is seen that the amount of non-bound water does not vary with the duration of freezing–thawing to a significant extent at an amide content of 33.5 mol%, and is decreased with freezing–thawing at amide content below 33.5 mol%. On the right-hand side of the two figures, more thermal treatment leads to more water

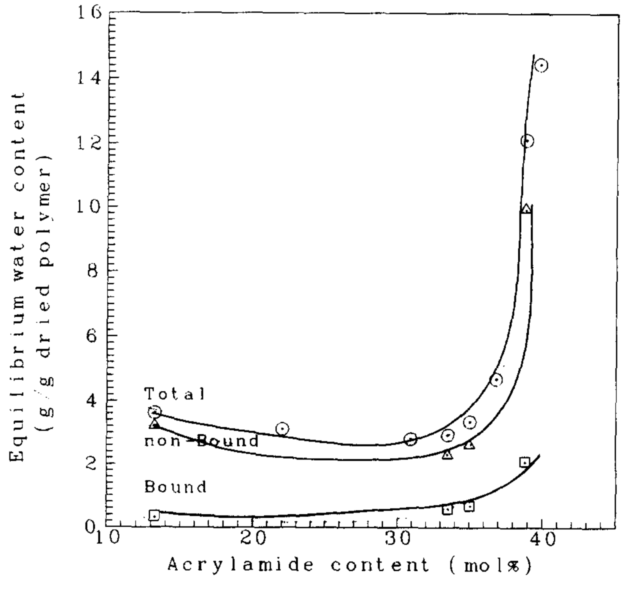

Figure 5 Composition dependence of amount of water in various states and water in total. All samples were treated with a 3-day freezing–thawing process

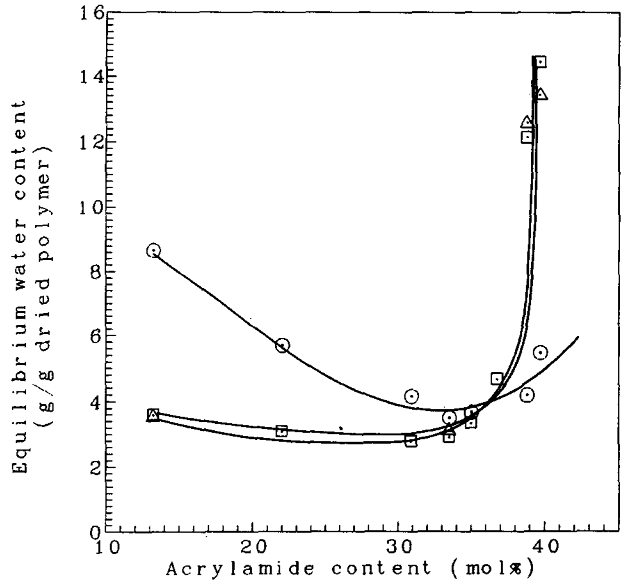

Figure 6 Variation of total water uptake with composition at various durations of freezing–thawing: (○) 1; (□) 3; (△) 7 days

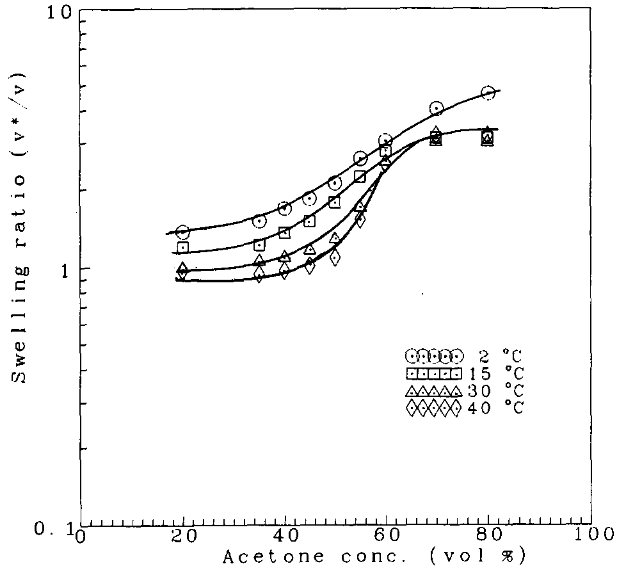

Figure 7 Volume phase transition diagram, presented as swelling ratio (V^*/V) *versus* acetone concentration in solutions, for sample TPH20. V^* and V are volume of the gel before and after the volume change at 30°C, respectively

uptake. The above complication demonstrates two opposite effects of duration of thermal cycling on water absorption, depending on the chemical compositions. More specifically, the thermal cycling causes simultaneously (1) the densification or crystallization of gels, and (2) the generation of a network defect or transition layer between phases. For gels with a lower content of amide, process (1) becomes more dominant, and non-bound water uptake of gels with higher content is controlled by the second process. The reduction of water uptake by freezing and thawing has been recognized for PVA gels[13], although the facilitation effect by freezing–thawing may also be possible for our samples.

To further illustrate the effect of freezing–thawing on water uptake, *Figure 6* shows total water uptake data for gels with 1, 3 and 7 days of freezing–thawing, indicating that once the freezing–thawing time is sufficiently long, say 3 days in this work, the water uptake varies very little with time. This might imply that the inhomogeneous structure of gels does not change at a freezing–thawing time greater than 3 days.

Phase transition and critical variables of gels

Figure 7 shows how the gel volume of sample TPH20 varies with the volume concentration of acetone (a poor solvent) in the acetone/water solutions in which gels were swollen. Starting from the lower side of the acetone concentration scale, the addition of acetone to solutions causes the polymer chains to come closer due to the increase of polymer–polymer affinity. This is seen from the shrinkage of volume with the addition of acetone in *Figure 7* at temperatures from 2 to 40°C. While the temperature is raised, the gel volume is increased at a fixed solution composition. This variation of gel volume with acetone concentration at various temperatures in *Figure 7* was also theoretically shown to exhibit a gradual change from a continuous type at lower temperatures to a stepwise character at higher temperatures[5,18].

The stepwise change on the gel volume–concentration–temperature plot is again illustrated for another sample, TPH16, in *Figure 8*. The two figures show that the volume change from a concentration of 40–60% at 40°C for TPH20 is more pronounced than that for TPH16. This is attributed to the difference in acid concentrations, or hydrogen ion pressure of gels, as reported in the literature[5]. It should be mentioned that gels with lower acid concentration, such as TPH8, TPH10, TPH12 and TPH13, did not experimentally show the stepwise transition over the temperature range from 20 to 70°C.

According to Tanaka[7], the critical endpoint (T_c) is the onset temperature during the heating or cooling process at which the phase transition phenomena start to disappear in *Figures 7* and *8*. It turns out that T_c is approximately 15°C for TPH20 and 40°C for TPH16. The limited data show the dependence of critical endpoint (temperature) on the chemical composition of gels.

Effect of temperature on swelling volume of gels

Figure 9 shows the temperature dependence of swelling ratio for five gels with increasing times of hydrolysis, in

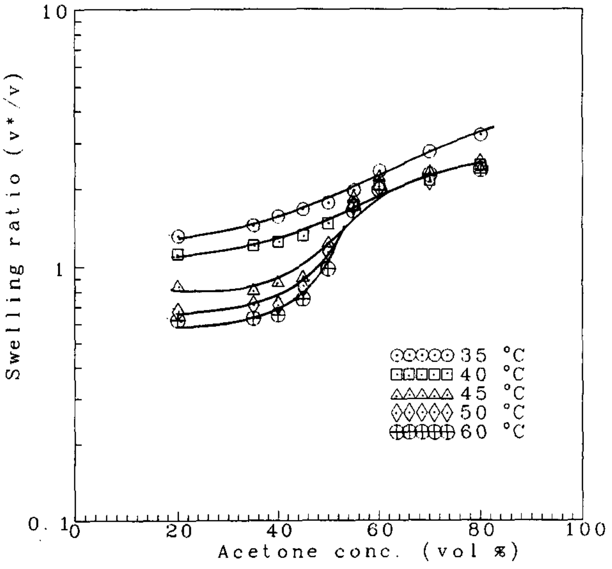

Figure 8 Volume phase diagram for sample TPH16 (see legend to *Figure 7*)

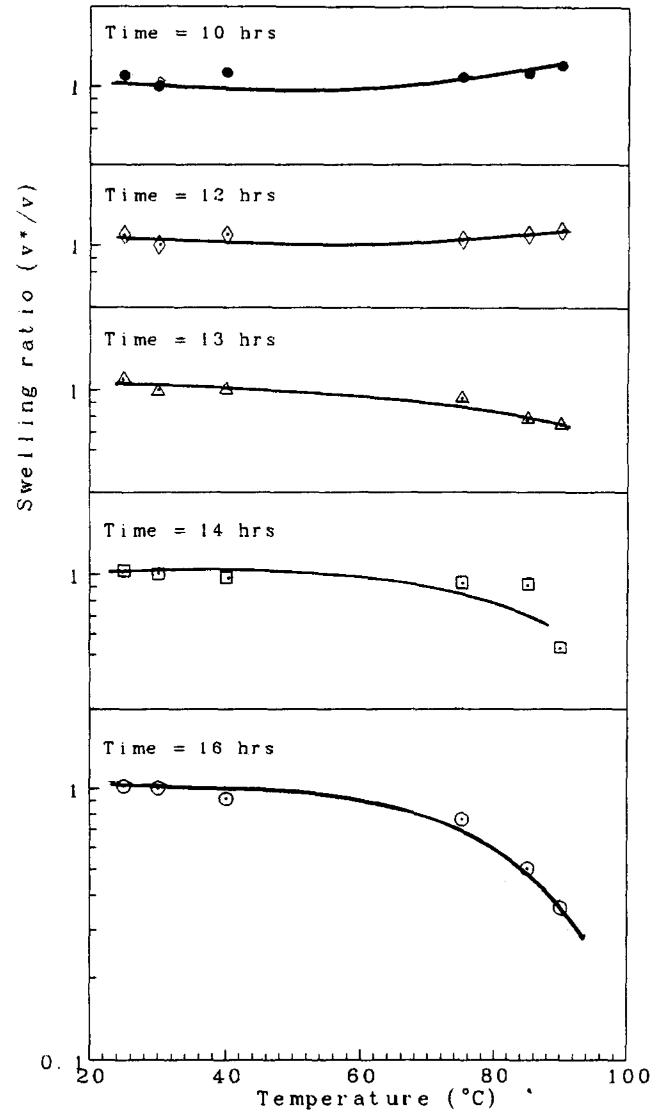

Figure 9 Temperature dependence of swelling ratio (V^*/V) for samples with various times of hydrolysis. V^* and V were taken at 30°C

which when the hydrolysis time is less than 13 h (content of acid <0.9 mol%) the gel volume drops with temperature. This dependence is not found, to our knowledge, for PAAm gels, and cannot be predicted by Tanaka's equation of state. This is because the increase of hydrophobic bonding with temperature leads to the increase of the contracting force[17,18], or the total osmotic pressure of the gels goes from zero to a negative value in response to temperature rise at initial temperatures greater than 75°C[6]. However, the volume of gels with hydrolysis time ⩾13 h shows an opposite temperature dependence in *Figure 9*, which is mainly caused by carboxyl moieties giving rise to an increase of hydrogen ion pressure and an increase of positive osmotic pressure with the increase of temperature over the temperature range from 60 to 90°C. At this juncture it is natural to reach an 'interpolated' result that the volume of the gel with hydrolysis time between 12 and 13 h maintains a constant value from 20 to 90°C, indicating its zero osmotic pressure over the whole temperature range.

Critical phenomena of water uptake

To further enhance the swelling–temperature data in *Figure 9*, the equilibrium water content (EWC) of gels is plotted against temperature for various gels in *Figure 10*. The temperature effect on EWC is of the same trend as that on gel volume: the EWC of gels with hydrolysis time >13 h is increased with temperature and that with hydrolysis time <12 h decreased. Again, the existence of a gel with the temperature-independent EWC from 10 to 60°C seems to be justified. According to the Gibbs–Helmholtz equation for EWC,

$$d\ln(\mathrm{EWC})/d(1/T) = -\Delta H_m/R \qquad (3)$$

where R is the gas constant, and ΔH_m the enthalpy of mixing between the dry polymer and an infinite amount of water. The two gels, TPH16 and TPH18, both exhibit increasing swelling with temperature as demonstrated in

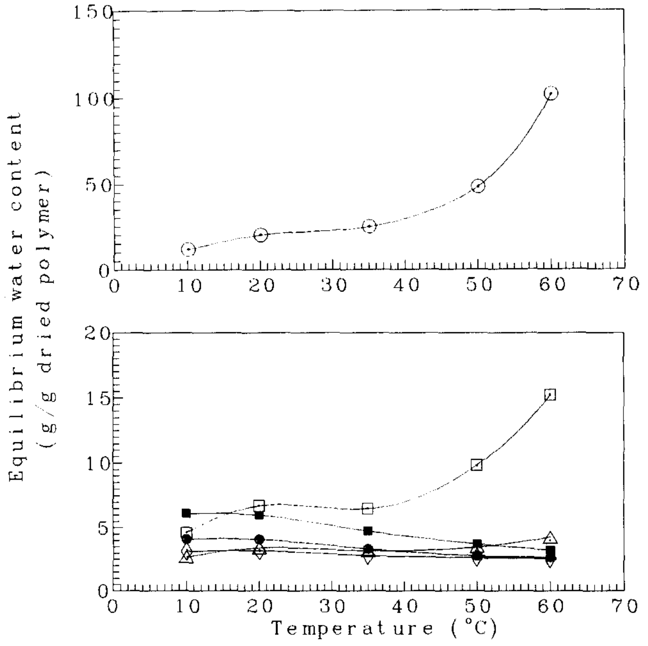

Figure 10 Temperature dependence of equilibrium water content (g water/g dry polymer) for samples with various times of hydrolysis: (○) 18; (□) 16; (△) 14; (◇) 12; (●) 10; (■) 8 h

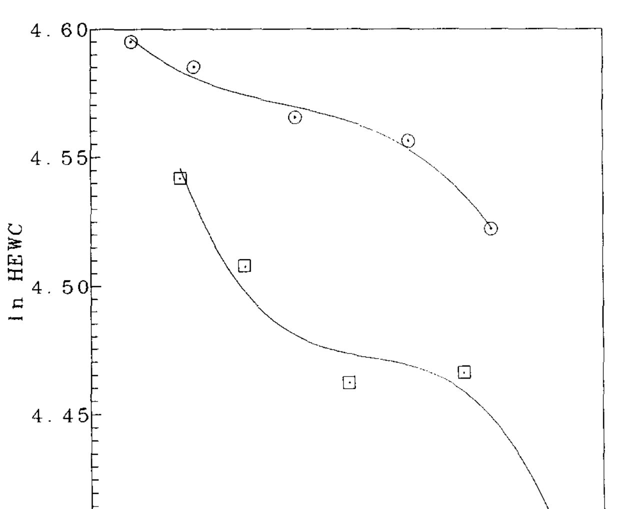

Figure 11 Plots of ln (equilibrium water content) *versus* the ratio of the critical temperature of sample to the temperature concerned (T_c/T) for two gels with acrylamide content (○) 38.80 and (□) 36.79 mol%

Figure 9 and *10*. With the aid of equation (3), the slopes of curves in *Figure 11* are equal to $(-\Delta H_m/R)/T_c$ in equation (3), showing endothermic mixing processes except at $T=T_c$. It is also inferred from *Figures 9* and *10* that the mixing is athermal for an 'ideal' gel with temperature-independent swelling, whose concentration of amide and acid groups is between those of TPH12 and TPH13. Clearly, gels with hydrolysis time greater than 13 h have the negative ΔH_m.

The positive temperature dependence of swelling for TPH16 and TPH18 is examined by plotting the logarithm of EWC *versus* the ratio of critical endpoint to temperature in *Figure 11*. Interestingly enough, the enthalpy of mixing between the dry polymer and water is not constant from 10 to 60°C, and slopes for the two curves tend to be zero at temperature equal to critical endpoint. TPH18 has higher enthalpic interactions between water and dry gel than TPH16, which has a lesser amount of amide/acid groups. Although the data are limited, this implies that the enthalpy of mixing is zero at critical points.

CONCLUSIONS

P(AN–AAm–AA) hydrogels were shown to exhibit positive or negative temperature dependence of volume and water content, depending on the chemical composition or the relative magnitudes of polymer–polymer affinity, rubber elasticity and hydrogen ion pressure. Moreover, the ideal gel with temperature-independent swelling was also demonstrated at AAm content = 33.5 mol% and AA content = 0.9 mol%. This ideal gel has the minimal affinity with water, as well as possessing the most dense structure. The athermal mixing occurring in the ideal gel over a rather wide range of temperature was also found for other gels at critical temperatures, in which the latter certainly need more experimental data to be verified. This ideal gel demonstrates the minimal contents of non-bound and total water, which are insensitive to the duration of freezing–thawing. However, the bound water in gels plays a minor role in total water uptake relative to unbound water, and its amount increases with the amide/acid components in polymers.

The effect of freezing–thawing on the water uptake may be positive or negative, depending on the regime of chemical compositions of polymers or whether crosslinking of chains or the network defect of gels is more significant in affecting the water retention behaviour. For the ideal gel, the chain crosslinking and network defects reach a balance. It is shown in this study that freezing–thawing strongly affects the inhomogeneous structure of gels, and the constant level for chain crosslinking and network defects is reached if the freezing–thawing time is sufficiently long.

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