



Phase transition of polyacrylamide gels in PEG solutions

Nilhan Kayaman,^a Oğuz Okay^{ab} & Bahattin M. Baysal^{ac*}

^aTUBITAK Marmara Research Center, Research Institute for Basic Sciences,
Department of Chemistry, PO Box 21, 41470 Gebze, Kocaeli, Turkey

^bKocaeli University, Department of Chemistry, Izmit, Kocaeli, Turkey

^cBoğazici University, Department of Chemical Engineering, 80815 Bebek, Istanbul,
Turkey

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ABSTRACT

Non-ionic polyacrylamide gels immersed in aqueous solutions of poly(ethylene glycol) (PEG) exhibit a continuous volume change upon continuous increase of the PEG concentration in the external solution. The volume change becomes discontinuous when ionizable groups are incorporated into the network. As the proportion of ionizable groups increases, or, as the molecular weight of PEG decreases, the critical concentration of PEG required for a discontinuous volume collapse rises. The distribution of PEG inside and outside the gel phase changes with gel volume; it also exhibits a discontinuous change at the phase transition. Flory–Huggins theory gives a qualitative description of the phenomenon. © 1997 Elsevier Science Limited

1 INTRODUCTION

Polymer gels are important materials of both fundamental and technological interests. In recent years, hydrophilic gels called hydrogels have received considerable attention for use as specific sorbents and as support carriers in biomedical engineering. Investigations of the swelling behavior of hydrogels in low molecular weight solvents have been reported in the last four decades. In more recent years attention has turned to the swelling and collapse phenomena that are observed when a hydrogel network is brought into contact with a solvent. The possibility of phase transitions has been predicted theoretically^{1–5} and proved experimentally

* To whom correspondence should be addressed.

on hydrolyzed polyacrylamide (PAAm) gels swollen in acetone–water mixtures.^{6–10} In such a transition, a change in a variable like pH, solvent composition or temperature can induce a discontinuous change in the volume of the swollen gel.^{11–13}

Although many studies have dealt with gels swollen in solvents, only a few were concerned with swelling in polymer solutions. The first theoretical studies on such (quasi)ternary systems assumed that the linear macromolecules cannot enter the gel phase.¹⁴ Others neglected the energetic interactions between the polymer and network segments.¹⁵ Recent experimental results indicate that these assumptions are unrealistic.^{16–18} Linear polymers can penetrate into the network depending on the thermodynamic parameters of the system, leading to the contraction of the gel. Since the linear polymer concentration inside the network depends on the size of the macromolecules, the gel excludes high molecular weight polymers. This characteristic of the gels is of pronounced practical interest; for example, polymeric gels can be used as extraction solvents to concentrate aqueous solutions of proteins or other biological systems.^{19–22} More recently, theoretical calculations using the classical Flory–Huggins theory predicted the possibility of a discontinuous phase transition in such systems, even for non-ionic gels.^{23,24} This prediction was proved with poly(*N*-isopropylacrylamide) (NIPA) gels swollen in aqueous poly(ethylene glycol) (PEG) solutions.²⁵

This paper presents the results of observations on PAAm gels immersed in aqueous solutions of PEG with molecular weights ranging from 194 to 35 000 g/mol. Here, we report the first observation of a discontinuous phase transition in ionic PAAm gels swollen in PEG solutions. The swelling behavior of PAAm gels as well as the PEG distribution inside and outside the gel phase were investigated as a function of the concentration and the molecular weight of PEG in the outer solution. We also give a qualitative interpretation of the swelling and absorption behavior of PAAm gels in polymer solutions in terms of the classical Flory–Huggins theory of the swelling equilibrium.

2 EXPERIMENTAL

2.1 Materials

PAAm gels were prepared by free-radical cross-linking copolymerization of acrylamide with a small amount of *N,N'*-methylenebis(acrylamide)

(Bis) in aqueous solution. Acrylic acid (Ac) was used as the ionizable comonomer. Ammonium persulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were, respectively, the initiator and the accelerator. The reactions were carried out at room temperature ($21 \pm 2^\circ\text{C}$), and the gels were prepared according to the following method.

Acrylamide (5 g), 133 mg Bis, 40 mg APS and varying amounts of Ac were dissolved in double-distilled water to give a total volume of 100 ml. To eliminate oxygen from the polymerization system, nitrogen was bubbled through the solution for 10 min. After addition of 0.24 ml of TEMED, the solution was transferred to small tubes of 5.8 mm in diameter. The gelation took place within 5 min. After 3 h, the gels were cut into specimens of approximately 10 mm in length and immersed in a large excess of distilled water for one day to remove the unreacted species. It was found that the sol fraction in the gels is less than 0.1% after extraction with water.

Reagent-grade PEGs were purchased from Fluka (PEG 300, 600, 1000, 1540, 2000 and 35000), Union Carbide Corp. (PEG 5000, 6000 and 20000), and Aldrich (tetraethylene glycol), and used without further purifications.

3 METHODS

3.1 Swelling measurements

The PAAm gel samples were immersed in vials (100 ml) filled with a PEG–water solution. The volume of solution in the vial was much larger than the gel volume so that the concentration of the solution was practically unchanged. The vials were set in a temperature-controlled bath at $25 \pm 0.1^\circ\text{C}$. In order to reach the equilibrium degree of swelling, the gels were immersed in solutions for at least one week. Two different methods were used to measure the equilibrium swelling ratio of the gels, V/V_0 , where V and V_0 are the volumes of gel at equilibrium and reference conditions, respectively. First, the diameter of the gels was measured by a calibrated digital compass and the swelling ratio was calculated as:

$$V/V_0 = (D/D_0)^3 \quad (1)$$

where D and D_0 are the diameter of the gels after equilibrium swelling and after synthesis, respectively. Second, the swelling ratio was determined

by weighing the specimens in the swollen and dry states. In order to dry the gel samples, they were first swollen in pure water and then successively washed with solutions whose composition were changed gradually from water to pure acetone. This solvent exchange process was used to facilitate final drying of the gel samples. The collapsed samples after the treatment with acetone as a final solvent were dried in a vacuum at 60°C to constant weight. The swelling ratio was calculated as:

$$V/V_0 = v_2^0 \left(1 + \frac{(q_w - 1)\rho}{d_1} \right) \quad (2)$$

where v_2^0 is the volume fraction of the network after preparation, q_w is the ratio of the weights of the network in the swollen state and the dry state, and ρ and d_1 are the densities of PAAm and PEG solution, respectively. Assuming additivity of the volumes of water, $d_w = 1$ g/ml, and PEG, $d_{\text{PEG}} = 1.1$ g/ml, and using the values $v_2^0 = 0.035$, $\rho = 1.42$ g/ml, the swelling ratios calculated using eqns (1) and (2) were found to be in good agreement. Each swelling ratio reported in this paper is an average of at least two separate measurements performed parallel using both methods; standard deviations of the measured swelling ratios were less than 10 and 5% of the mean for swollen and collapsed gels, respectively.

3.2 Absorption measurements

The PEG concentration inside the gel samples was measured by refractometry using an Abbe refractometer at 20°C as follows. After removing the gel samples from the aqueous solutions of PEG, their surfaces were washed quickly with pure water and then the PEG chains inside the gels were extracted using distilled water as the extraction solvent at room temperature. Usually, for gel samples of about 3 ml in volume, a total amount of 30 ml of water was used for the extraction experiments. Each extraction process took one week, during which the solvent was refreshed at least three times until the PEG concentration in the solution decreases to 1/10 of the initial value. At this PEG concentration level, the amount of PEG inside the gel that cannot be leached into the solution phase causes a maximum error in the final results of less than 4%. The amount of extracted PEG was measured by refractometry using calibration curves prepared for each PEG sample. All measurements were performed in duplicate; standard deviations of the measured PEG distributions were generally less than 5% of the mean.

4 RESULTS

4.1 Non-ionic gels

The variation of the degree of swelling of the non-ionic PAAm gel, V/V_0 , with the volume fraction of PEG in the external solution, ϕ , is shown in Fig. 1. The molecular weights of PEG used were between 300 and 6000 g/mol. For high molecular weight PEGs, measurements at high polymer concentrations could not be carried out because they were not soluble. Experimental data are shown as symbols. The dotted curves were calculated using the Flory–Huggins theory as discussed in the next section. The PAAm gel without any ionizable groups exhibits a continuous change in the swelling volume over the entire concentration and molecular weight ranges. This behavior is in contrast to NIPA gels which undergo a discontinuous phase transition at PEG molecular weights of 200 and 1000.²⁵ Figure 1 also shows that, as the PEG concentration outside the gel phase increases, the volume of the gel decreases. Furthermore, at high PEG molecular weights, the swelling ratio becomes rather insensitive to the molecular weight of the linear polymer. This feature is better seen in Fig. 2 which illustrates the dependence of the swelling ratio on the molecular weight of PEG for fixed concentration of PEG in the external solution. For molecular weights of PEG higher than 2000 g/mol, the swelling ratio is independent of the molecular weight within the limits of

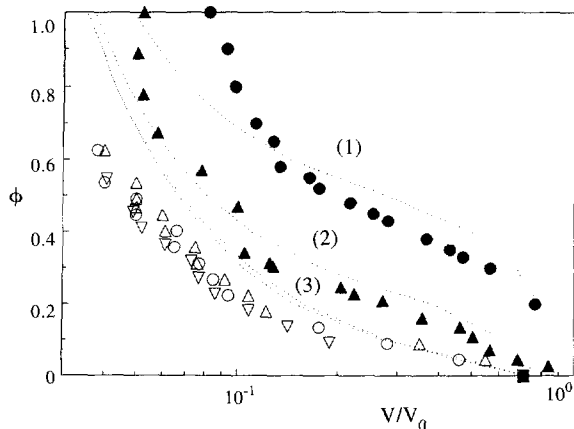


Fig. 1. Variation of the swelling ratio V/V_0 of the non-ionic PAAm gel with the concentration of PEG in the outer solution. Each PEG concentration is given as volume fraction in the solution phase ϕ . PEG300 (\bullet); PEG 600 (\blacktriangle); PEG 1540 (\triangle); PEG 2000 (\circ); and PEG 6000 (∇). The curves were calculated using eqns (7)–(9) for the molecular weights 300 (1); 600 (2); and 2000–20 000 g/mol (3).

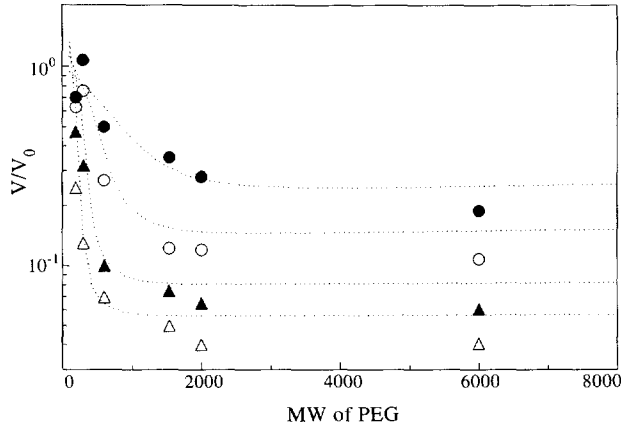


Fig. 2. Variation of the swelling ratio V/V_0 of the non-ionic PAAm gel with the molecular weight of PEG. The volume fraction of PEG in the outer solution = 0.10 (\bullet); 0.20 (\circ); 0.40 (\blacktriangle); and 0.60 (\triangle). The curves were calculated using eqns (7)–(9).

experimental error. In Fig. 3, the PEG distribution inside and outside the gel phase is shown as a function of the PEG concentration in the solution. Here v_3/ϕ represents the ratio of the volume fraction of PEG in the gel phase (v_3) to that in the solution phase (ϕ); thus $v_3/\phi = 1$ means that the PEG concentration inside the gel is equal to that in the solution whereas $v_3/\phi = 0$ means that the gel excludes all the PEG molecules. Figure 3 indicates that a large amount of PEG can penetrate into the gel if the

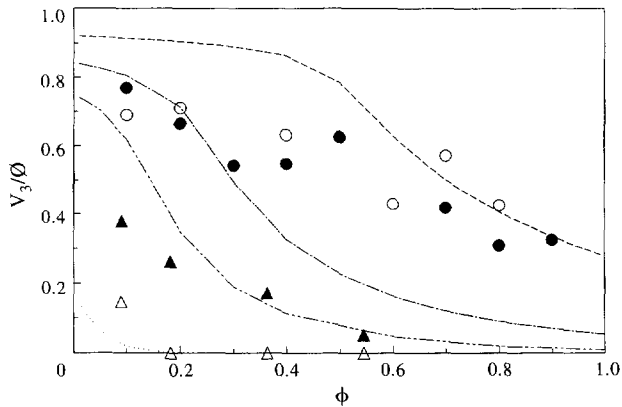


Fig. 3. Dependence of the PEG distribution inside and outside the gel phase, v_3/ϕ , on the PEG concentration in the solution. PEG 300 (\bullet); PEG 600 (\circ); PEG 1000 (\blacktriangle); and PEG 6000 (\triangle). The curves were calculated using eqns (7)–(9).

PEG chains are short enough ($M = 300\text{--}600\text{ g/mol}$). Increasing the volume fraction ϕ or molecular weight M of PEG in solution decreases the v_3/ϕ ratio and it approaches zero within experimental accuracy for $M = 6000\text{ g/mol}$ and $\phi > 0.20$. Thus, if the molecular weight of PEG is sufficiently high the linear polymer does not penetrate inside the PAAm network.

4.2 Ionic gels

Ionic gels were made using acrylic acid as a comonomer in the synthesis of PAAm gels. In Fig. 4 the swelling ratio of gels containing varying amounts of acrylic acid with respect to the dry copolymer is plotted as a function of the PEG 300 concentration in the outer solution. As expected, the swelling ratio in a given PEG–water mixture increases with increasing acrylic acid content. At low PEG concentrations the PAAm gels are swollen, at high concentrations the gels are collapsed. However, for acrylic acid contents higher than a certain value (28%) the gels remain in the swollen state over the entire range of the external PEG concentration. For the ionic gels shown in Fig. 4 with 6–22% acrylic acid (in the dry copolymer), the dependence of PEG concentration on the swelling ratio exhibits a discontinuity. In the concentration range marked with horizontal dotted lines, both a swollen and a collapsed state can be observed but

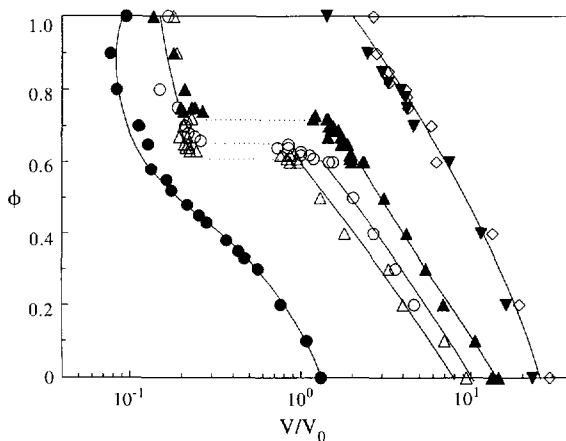


Fig. 4. Variation of the swelling ratio V/V_0 of ionic PAAm gels with the concentration of PEG 300 in the outer solution. Acrylic acid (Ac) content of the dry copolymer = 0 (\bullet); 6 (Δ); 13 (\circ); 22 (\blacktriangle); 28 (\blacktriangledown); and 40 w/w% (\diamond). The solid curves only show the trend of data. The dotted horizontal lines illustrate the phase transition regions.

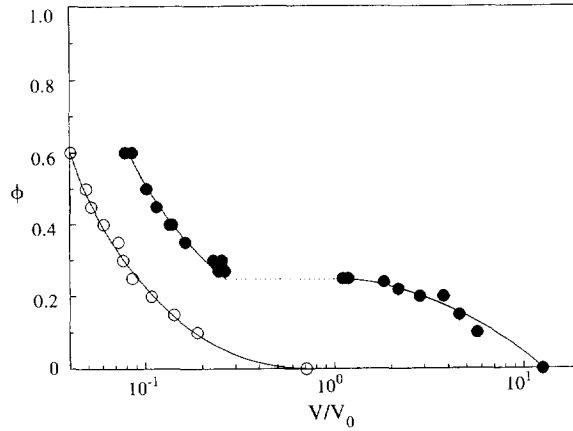


Fig. 5. Variation of the swelling ratio V/V_0 of PAAm gels with the concentration of PEG 6000 in the outer solution. Ac = 0 (○); and 13 w/w% (●).

never an intermediate state. When a collapsed gel is placed in a PEG solution with a concentration below this value, the gel re-swells. These findings indicate a first-order transition. The jump of the network volume occurs at the critical volume fraction of PEG $\phi = 0.625$, 0.655 and 0.735 for 6, 13 and 22% acrylic acid, respectively. Thus, the critical value of ϕ at which transition takes place increases with increasing ionic group content of the network. Also, the magnitude of the collapse becomes larger as the ionic group content of the network increases. Figure 5 compares the swelling behavior of ionic and non-ionic gels in PEG 6000 solutions. In the non-ionic gels, the contraction of polymer networks in PEG 6000–water mixture occurs smoothly but it is jumpwise first-order phase transition in ionic gels with the jump at $\phi = 0.26$ for 13% acrylic acid, which is much lower than that observed in PEG 300–water mixtures (Fig. 4). In Fig. 6(a) and 6(b), the swelling ratio of ionic gels containing a fixed amount of acrylic acid is plotted as a function of the PEG concentration for various PEG molecular weights. One can see that the critical value of ϕ required for a discontinuous volume collapse is 0.655 , 0.45 , 0.395 , and 0.26 respectively for PEG molecular weights 300, 1000, 2000, and 6000 (Fig. 6(a)). Thus, the critical volume fraction of PEG is shifted towards lower values as the molecular weight of PEG in the outer solution increases. However, in aqueous solutions of PEG with molecular weights higher than 20 000 g/mol, or in tetraethylene glycol–water mixtures, the gel changes its volume continuously (Fig. 6(b)), indicating that a jumpwise collapse of the gel volume only takes place within a certain molecular weight range of the linear chains. The distribution of PEG inside and outside the gel phase for the gels shown in Fig. 6(a) is given in Fig. 7. A

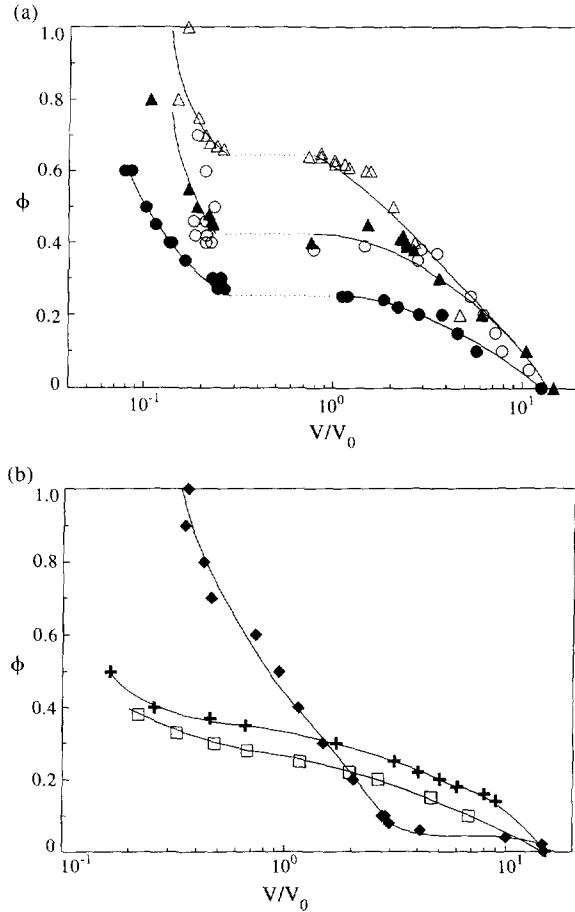


Fig. 6. Swelling ratio V/V_0 of the ionic PAAm gel with 13 w/w% Ac content shown as functions of the concentration of PEG in the outer solution. The experimental data are shown as symbols. The curves only show the trend of data. (a) PEG 300 (Δ); PEG 1000 (\blacktriangle); PEG 2000 (\circ); and PEG 6000 (\bullet). (b) PEG 194, i.e. tetraethylene glycol (\blacklozenge); PEG 20000 ($+$); and PEG 35000 (\square).

jumpwise decrease in the content of PEG in the gel phase is observed at the critical ϕ ranges at which the gel shrinks discontinuously.

It is also interesting to compare the degree of swelling of ionic PAAm gels immersed in solutions of linear polymers of different molecular weight. We expect that the smaller the linear chains in the external solution, the higher the extent of swelling of the gel due to the effect of mixing entropy of linear polymers. This is, with one exception, indeed so. Only the swelling behavior of PAAm gels in tetraethylene glycol (TEG) solutions exhibits an unusual feature. One can see from Fig. 6(b) that the gel shrinks in TEG solutions first abruptly in a relatively narrow

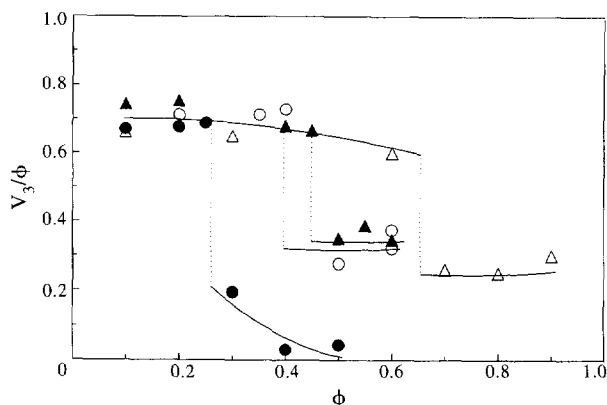


Fig. 7. Dependence of the PEG distribution inside and outside the ionic PAAm gel with 13 w/w% Ac content, v_3/ϕ , on the PEG concentration in the solution. PEG 300 (Δ); PEG 1000 (\blacktriangle); PEG 2000 (\circ); and PEG 6000 (\bullet). The curves show the trend of the data.

concentration range (between 0 and 10% TEG) but then, in the large region of TEG concentration, the gel deswells only slightly. Furthermore, PAAm gels in TEG–water mixtures with $\phi < 0.20$ swell less than in corresponding high molecular weight PEG–water mixtures.

5 DISCUSSION

There are two possible reasons for the contraction of PAAm gels immersed in PEG solutions: (1) complex formation between the PAAm and PEG chains, and (2) osmotic deswelling of the gel in the polymer solution. In the first case, a complex between two polymers may form due to hydrogen bonding. Such a complex is expected to be much more hydrophobic than the polymer chains taken separately.^{26,27} As a result, increasing PEG concentration in the solution increases the polymer content inside the gel phase so that the network becomes more hydrophobic and it collapses in water solutions. Polycarboxylic acids such as poly(methacrylic acid) (PMAA) or poly(acrylic acid) (PAA) have long been known to form complexes with PEG under appropriate conditions of pH.^{28–33} The formation of intermolecular complexes between PMAA gel and PEG is also a well known phenomenon and results in the collapse of the gel.³⁴ The complexation results from cooperative hydrogen bonding between long sequences of carboxy groups and ether oxygen atoms at low pH. However, the stability of such complexes decreases sharply with the decrease of the degree of polymerization of PEG chains or with the

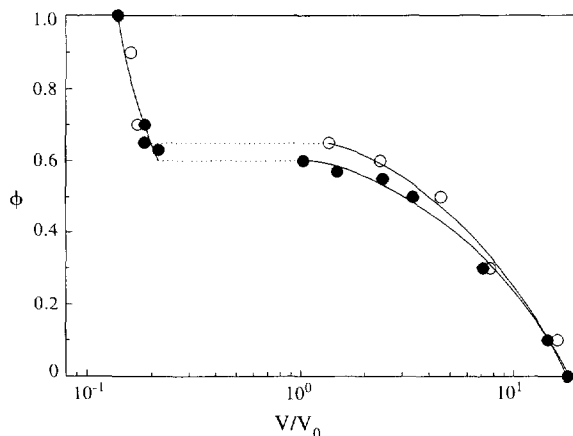


Fig. 8. Swelling ratio V/V_0 of the ionic PAAm gel with 13 w/w% Ac content shown as functions of the concentration of PEG in the outer solution. pH of the polymer solution = 6.5–7 (•) and 9 (○).

increase of the pH of the solution. For instance, PEG with molecular weight of 7500 or lower does not form a complex with PAA.^{35,36} Moreover, since complexation is produced only by carboxylic groups in the undissociated state, complexation is possible in the low pH region. As it was indicated earlier, even at pH = 2, there is no complexation between PAA and PEG when the molecular weight of PEG is 1500 or lower.³⁷ On the other hand, at low pH, the undissociated acid groups can also interact with the amide groups to form PAAm–PAA complexes through hydrogen bonds.³⁸ In the present study, the aqueous solutions of PEG exhibited a pH value not less than 6.5. Thus, it is reasonable to assume that the contraction of the gel in PEG solutions is due to the osmotic deswelling of the gel (no complex formation).³⁹ That assumption is consistent with the observations of the swelling behavior of the ionic gels in PEG solutions of different pH. Figure 8 compares the swelling behavior of an ionic gel in PEG 600 solutions. Filled and empty circles represent the results of swelling measurements carried out at pH = 6.5–7 (without addition of NaOH) and at pH = 9 (in the presence of NaOH), respectively. The critical value of ϕ increases and the magnitude of the collapse becomes larger as the pH of the polymer solution increases. If the complexation were the reason of the polymer collapse, increasing pH would prevent the collapse of the gel due to the excessive osmotic pressure in the swollen gel produced from the dissociation of carboxylic acid groups of the network chains. However, Fig. 8 shows the opposite behavior.

To interpret the experimental data in the previous section, we use the classical Flory–Huggins (FH) theory of swelling equilibrium. However,

FH theory does not account for free-volume effects or hydrogen bonding interactions, and thus cannot describe quantitatively the swelling behavior of hydrogels. Although some lattice models have been proposed recently to account for these interactions,^{40–42} these models are more complex mathematically than the FH theory and require several adjustable parameters to apply the actual systems. We will adopt here the FH theory for a qualitative understanding of the experimental findings.

Swelling of a polymer network is governed by at least three free energy terms, i.e. the changes in the free energy of mixing ΔG_m , in the free energy of elastic deformation ΔG_{el} , and in the free energy of electrostatic interactions ΔG_i :

$$\Delta G = \Delta G_m + \Delta G_{el} + \Delta G_i \quad (3)$$

According to the Flory–Huggins theory, ΔG_m is given by:⁴³

$$\Delta G_m = RT \left(\sum_i n_i \ln v_i + \sum_{i < j} n_i v_i \chi_{ij} \right) \quad (4)$$

where n_i is the moles of the species i , v_i is its volume fraction, χ_{ij} is the interaction parameter between the species i and j , R is the gas constant and T is the temperature. For the present ternary system, the subscript $i = 1, 2$, and 3 denotes the solvent, the network, and the linear polymer, respectively. For the free energy of elastic deformation, ΔG_{el} , several theories are available.^{44–52} However, we will use here the simplest affine network model to describe qualitatively the behavior of PAAm gels:⁴³

$$\Delta G_{el} = (3/2)(RT/NV_1)((v_2^0/v_2)^{2/3} - 1 - \ln(v_2^0/v_2)^{1/3}) \quad (5)$$

where N is the average number of segments in the network chains, V_1 is the molar volume of solvent and v_2 is the volume fraction of polymer network in the equilibrium swollen gel. Use of other elastic free energy equations^{44–52} does not affect the results of the present study. It must be noted, however, the validity of eqn (5) or any similar equation for gels containing dissolved polymer is unknown. Interchain entanglements between the network and PEG chains should be mentioned as the possible source of error with the use of eqn (5) for the present system. For weakly charged ionic gels, the free energy of electrostatic interactions ΔG_i may be written as follows:⁴³

$$\Delta G_i = RT \frac{f v_2}{N v_1} n_i \ln(fv_2/N) \quad (6)$$

where f is the average number of ionic units in a network chain.

Substitution of eqns (4)–(6) into eqn (3) and differentiating with respect to the number of moles of solvent n_1 and polymer molecules n_3 yields the following set of equations for the excess chemical potentials of the solvent and the polymer in both gel and solution phases:

$$\frac{\Delta\mu_1^{\text{gel}}}{RT} = N^{-1}(v_2^{1/3}v_2^{0.23} - v_2/2) + \ln v_1 + (1 - v_1) - v_3/y + (\chi_{12}v_2 + \chi_{13}v_3) \\ \times (1 - v_1) - \chi_{23}v_2v_3 - v_2f/N \quad (7a)$$

$$\frac{\Delta\mu_1^{\text{sol}}}{RT} = \ln(1 - \phi) + \phi(1 - 1/y) + \chi_{13}\phi^2 \quad (7b)$$

$$\frac{\Delta\mu_3^{\text{gel}}}{yRT} = N^{-1}(v_2^{1/3}v_2^{0.23} - v_2/2) + (1/y)\ln v_3 + (1/y)(1 - v_3) - v_1 \\ + (\chi_{13}v_1 + \chi_{23}v_2)(1 - v_3) - \chi_{12}v_1v_2 - v_2\frac{f}{N} \quad (8a)$$

$$\frac{\Delta\mu_3^{\text{sol}}}{yRT} = (1/y)\ln\phi - (1 - \phi) + (1/y)(1 - \phi) + \chi_{13}(1 - \phi)^2 \quad (8b)$$

where y is the number of segments in the linear polymer and ϕ is its volume fraction in the solution phase. The state of equilibrium swelling of a network immersed in a polymer solution is obtained when the solvent and the polymer inside the network are in thermodynamic equilibrium with those outside. This equilibrium state is described by the equality of the chemical potential μ of these components in both phases. Thus, at swelling equilibrium, we have:

$$\Delta\mu_1^{\text{gel}} - \Delta\mu_1^{\text{sol}} = 0 \quad (9a)$$

$$\Delta\mu_3^{\text{gel}} - \Delta\mu_3^{\text{sol}} = 0 \quad (9b)$$

In terms of the osmotic pressure π , eqn 9(a) can also be written as:

$$\pi = -\frac{(\mu_1^{\text{gel}} - \mu_1^{\text{sol}})}{V_1} = 0 \quad (9a')$$

Osmotic pressure π of a gel determines whether the gel tends to expand or to shrink. When non-zero, π provides a driving force for gel volume change. Solvent moves into or out of the gel until π is zero, i.e. until the forces acting on the gel are balanced.

The system of equations represented by eqn (9) has been solved numerically to calculate the swelling ratio of PAAm gels in aqueous PEG solutions ($V/V_0 = v_2^0/v_2$) and the ratio of PEG concentrations inside and outside the gel phase (v_3/ϕ). For calculations, the values used were $v_2^0 = 0.035$ (estimated assuming additivity of the volumes of water and PAAm, $\rho = 1.42$ g/ml), $\chi_{12} = 0.48$,⁵³ and $\chi_{13} = 0.45$.⁵⁴ The number of segments in a network chain N was estimated from the swelling ratio of the non-ionic gel in pure water and using eqn 7(a) for the condition $v_3 = 0$ and $\Delta\mu_1^{\text{gel}} = 0$. The value $v_2 = 0.049$ found by experiments yielded $N = 165$. N was held constant at this value in the calculations described here. It was also assumed that y is equal to the degree of polymerization of the PEG chains. The only unknown parameter χ_{23} was taken as a model parameter. The value $\chi_{23} = 0.17$, providing a best fit to the experimental swelling data obtained with non-ionic gels swollen in PEG 300 solutions, was used throughout this study. For ionic gels and for certain values of ϕ , eqn (9) is satisfied by three values of both v_2 and v_3 , indicating the coexistence of two gel phases with different conformations and appearance of van der Waals loop in the swelling curves. In these cases, the composition of the gels in coexisting phases was calculated by equating chemical potentials of the network chains in both gel phases.

The dotted curves in Figs 1–3 were calculated using eqn (9). Theoretical V/V_0 and v_3/ϕ values are in agreement with the experimental data indicating that eqns (7) and (8) describe semi-quantitatively the swelling and absorption behaviour of the non-ionic PAAm gels in PEG solutions. The FH theory predicts every trend observed by experiments. According to eqn (7b), increase in the concentration of PEG ϕ leads to decreasing chemical potential of the solvent in the outer solution. This causes a lowering of the osmotic pressure in the swollen gel and to the shrinkage of the gel. The ratio v_3/ϕ is always less than unity, i.e. the concentration of PEG chains inside the gel is always lower than in the outer solution. This is due to the loss in conformational entropy of PEG chains penetrating the gel as well as due to the repulsion between network and polymer segments represented by the value χ_{23} . This concentration difference of PEG between the inside and outside the gel leads to an additional osmotic pressure compressing the network. This effect becomes more pronounced as the concentration or the degree of polymerization of PEG in the external solution increases. If the molecular weight of PEG is sufficiently high, PEG does not penetrate inside the network and create strong exterior pressure.

Results of calculations for ionic gels are presented in Figs 9 and 10. The size of ionic gels in the swollen state is much larger than that of a neutral network because of the additional swelling due to the osmotic pressure of

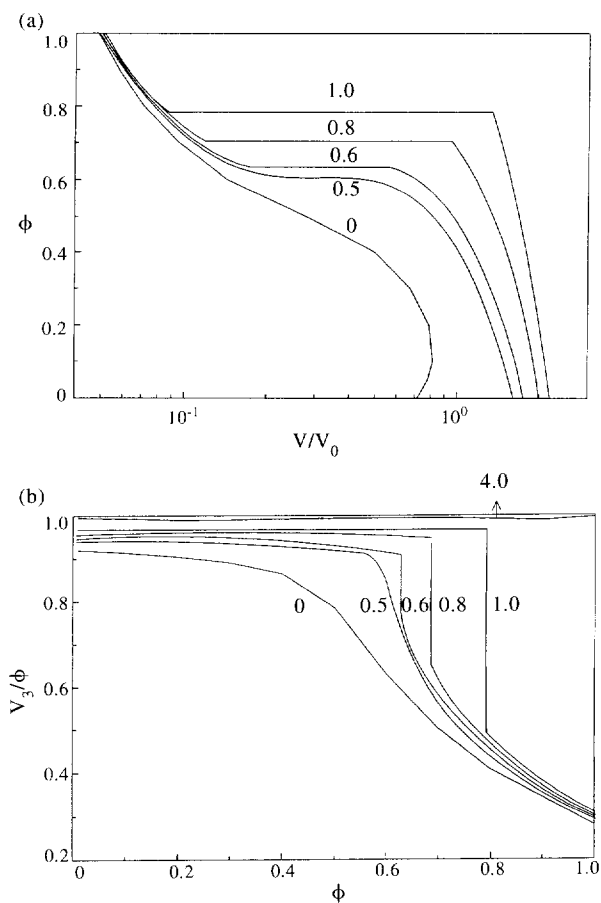


Fig. 9. PEG 300 concentration versus swelling (a) and absorption ratio plots (b), V/V_0 and v_3/ϕ respectively, for a series of values of f , which is proportional to the amount of ionizable group incorporated into the network. Calculations from eqns (7)–(9) for $y = 6.4$.

counterions. Therefore, PEG chains can penetrate the swollen ionic gels without essential loss in conformational entropy. In Fig. 9(a) and (b), ϕ versus V/V_0 and v_3/ϕ plots are shown for PEG 300–water mixtures and for a series of values of f , which is proportional to the amount of ionizable group incorporated into the network. A discrete first-order phase transition is observed only if f exceeds a critical value. As f increases, the jump in V/V_0 and v_3/ϕ moves to higher concentrations of linear polymer in the outer solution and the magnitude of the collapse becomes larger, as was found experimentally in the previous section. If f is sufficiently high, the gel remains in the swollen state over the entire range of PEG concentration and the solution compositions inside and outside the gel become practically identical. Calculated results for gels containing a fixed amount

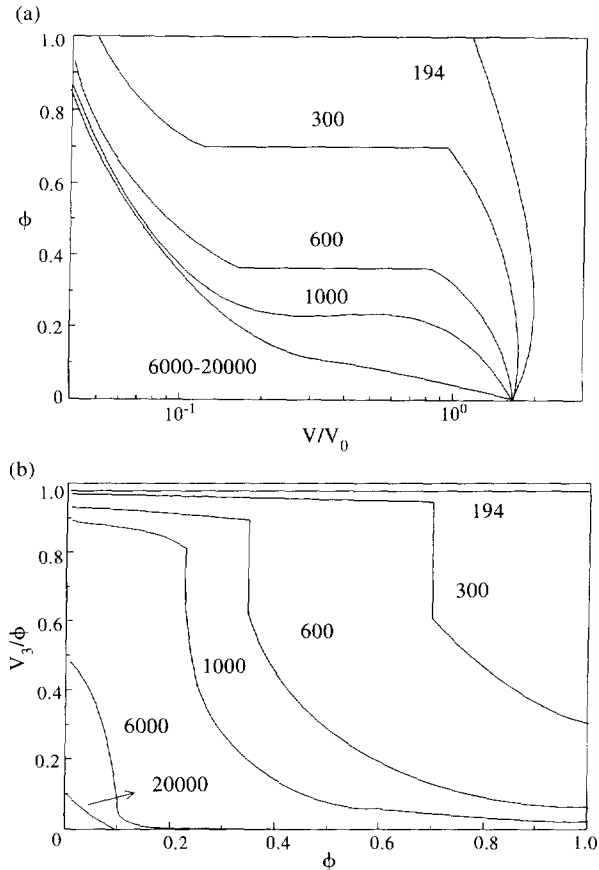


Fig. 10. Swelling (a) and absorption ratios (b), V/V_0 and v_3/ϕ , respectively, for an ionic PAAm gel as functions of PEG concentrations for different PEG molecular weights. Calculations from eqns (7)–(9) for $f = 0.8$.

of ionic groups are presented in Fig. 10(a) and (b). Here, ϕ versus V/V_0 and v_3/ϕ plots are shown for different PEG molecular weights. The discrete phase transition takes place over a small range of PEG molecular weight. Similar to the ionic-group effect, decreasing molecular weight of PEG shifts the critical concentration to higher values, in qualitative agreement with the experimental data shown in Figs 6 and 7.

Discrepancies between calculated and measured swelling behavior are apparent for tetraethylene glycol (TEG) solutions. Calculated results indicate that the PAAm gels remain in the swollen state over the whole concentration range of TEG (Fig. 10(a), the curve with $M = 194$). In contrast, experimental data show a rapid decrease of the gel volume up to 10% TEG concentration, and then the gel shrinks only slightly with increasing concentration (Fig. 6(b)). This unusual feature may be due to

the action of TEG as an organic solvent rather than a linear chain. Thus, the addition of a small amount of TEG into water may result in the destruction of the solvation structure of water molecules around amide groups of the network chains, and so the association of the dehydrated chains results in smaller gel volumes than those in polymer solutions of higher molecular weight.

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