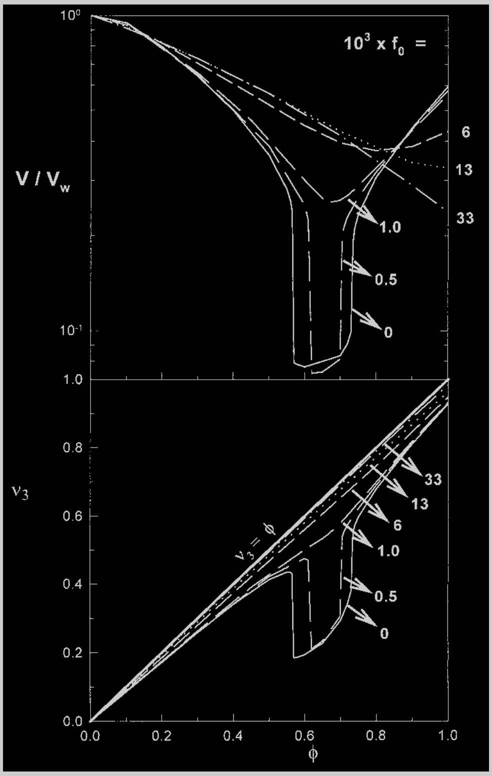
Full Paper: The swelling behavior of a series of strong polyelectrolyte hydrogels based on *N*-isopropylacrylamide (NIPA) and 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) was investigated in aqueous solutions of poly(ethylene glycol)s (PEG) of molecular weights 300 and 400 g/mol. Non-ionic hydrogels or hydrogels with 1 mol-% AMPS deswell with increasing PEG-300 volume fraction ϕ in the external solution up to $\phi = 0.6$. As ϕ is further increased, the hydrogels start to swell up to $\phi = 1$. The distribution of PEG inside and outside the gel phase changes with the gel volume; PEG chains first move from the gel to the solution phase from $\phi = 0$ to 0.6, while at higher ϕ values they again penetrate the gel phase. In PEG-400 solutions, the contraction of the gels is jumpwise first-order phase transition at a critical ϕ, while their reswelling occurs smoothly at higher values of ϕ. Calculations using the Flory-Huggins theory indicate attractive interactions between PEG and PNIPA segments, which are responsible for the observed reentrant transition behavior.



Variations of the swelling ratio (V/V_w) and the PEG concentration inside the PNIPA gels (v_3) with the concentration of PEG-300 in the outer solution ϕ. Calculations were using the FH theory for a series of values of f_0, which is proportional to the amount of ionizable group incorporated into the network.

Reentrant Phase Transition of Strong Polyelectrolyte Poly(*N*-isopropylacrylamide) Gels in PEG Solutions

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Introduction

Swelling behavior of polymeric gels in low molecular weight solvents has been studied repeatedly over the last four decades. However, only a few researchers were concerned with swelling in polymer solutions.[1–11] Recently, we have reported swelling behavior of both weak- and strong-polyelectrolyte poly(acrylamide) (PAAm) hydrogels in aqueous solutions of poly(ethylene glycol)s (PEG) as well as PAAm's of various molecular weights.[12–15] As predicted theoretically,[16] we observed a first-order volume phase transition in ionic PAAm hydrogels immersed in PEG solutions, if both the chain length and the concentration of PEG in the external solution assume critical values.[12, 15] These experimental findings can be explained semi-quantitatively within the framework of the classical Flory-Huggins (FH) theory.[14, 15] Calculations indicate that the collapse of polymer gels in polymer solution is due to the formation of ion pairs inside the gel, which is pronounced in concentrated polymer solutions having very low dielectric constant compared to that of water.[15]

Poly(*N*-isopropylacrylamide) (PNIPA) gel is a well known temperature-sensitive gel exhibiting swelling or deswelling transition at about 34 °C in water.[17] Moreover, an unusual feature of the swelling behavior of PNIPA gels is a reentrant phenomenon where the gels collapse once and reswell as a particular external condition is varied

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monotonically.[18] The reentrant phase transition in PNIPA gels has been observed in solvent mixtures such as water-dimethylsulfoxide (DMSO),[18, 19] water-methanol,[20] water-ethanol,[20] or water-PEG-200 mixtures.[21] In these ternary systems, the gel first collapses then reswells if the composition of the solvent mixture is continuously varied.

In the present work, we investigated the swelling behavior of strong polyelectrolyte PNIPA gels in aqueous solutions of PEG of molecular weights 300 and 400 g/mol and compared the experimental results with those obtained using PAAm gels. For this purpose, 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) was used as the ionic comonomer of NIPA between 0 and 10 mol-%. As will be shown below, PNIPA gels in PEG-300 or PEG-400 solutions exhibit a reentrant transition behavior at low ionic group (AMPS) contents, whereas for AMPS contents higher than a certain value the gels remain in the swollen state over the entire range of the external PEG concentration. Calculations indicate attractive interactions between PEG and PNIPA compared to the repulsive interactions between PEG and PAAm segments, which are responsible for the different swelling behavior of PNIPA and PAAm gels in aqueous PEG solutions.

Experimental Part

Materials

N-isopropylacrylamide (NIPA, Aldrich) was used as received. 2-acrylamido-2-methylpropane sulfonic acid (AMPS-H$^+$, Merck) was crystallized from boiling methanol. 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) stock solution was prepared by dissolving 20 g of AMPS-H$^+$ in about 40 mL of distilled water and adding to this solution 10 mL of a 30% NaOH solution under cooling. Next, the solution was titrated with 1 M NaOH to pH = 7.00 and finally, the volume of the solution was completed to 100 mL with distilled water. 1 mL of AMPS stock solution thus prepared contained 0.996 mmol AMPS. *N,N′*-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and *N,N,N′,N′*-tetramethylethylenediamine (TEMED) were used as received. A stock solution containing NIPA and BAAm was prepared by dissolving 4 g of NIPA and 0.064 g of BAAm in 50 mL of distilled water. Distilled and deionized water was used for the swelling experiments. For the preparation of the stock solutions and for the hydrogel synthesis, distilled and deionized water was distilled again prior to use and cooled under nitrogen bubbling. Reagent-grade poly(ethylene glycol)s (PEGs) were purchased from Fluka (PEG-300 and PEG-400, where the number indicates its molecular weight), and used without further purifications.

Synthesis of Hydrogels

PNIPA gels were prepared by free-radical crosslinking copolymerization of NIPA with a small amount of BAAm in aqueous solution at 5 °C in the presence of 3.51 mM APS as the initiator. AMPS was used as the ionic comonomer of NIPA. Both the crosslinker ratio (mole ratio of the crosslinker BAAm to the monomers) and the total monomer concentration were fixed at 1/82 and 0.700 M, respectively, whereas the ionic comonomer AMPS content of the monomer mixture was varied from 0 to 10 mol-%. To illustrate the synthetic procedure, we give details for the preparation of the hydrogel with 1 mol-% AMPS in the comonomer feed composition:

NIPA-BAAm stock solution (9.8 mL), AMPS stock solution (0.07 mL) and APS (0.008 g) were mixed and completed to 10 ml with distilled water. After bubbling nitrogen for 20 min, TEMED (0.025 mL) was added to the mixture. The solution was then poured into several glass tubes of 4.5–5 mm internal diameters and about 100 mm long. The glass tubes were sealed, immersed in a thermostated water bath at 5 °C and the polymerization was conducted for one day. Both the gel fraction and the monomer conversion measurements[22] showed that the reaction is complete after one day of crosslinking copolymerization. After the reaction, the hydrogels were cut into specimens of approximately 10 mm in length and immersed in a large excess of distilled water for 1 day to remove the unreacted species.

Swelling Measurements

Swelling experiments were carried out at 25 ± 0.1 °C or at 18 ± 0.1 °C in the aqueous solutions of PEG- 300 and PEG-400 of various concentrations. The hydrogel 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. In order to reach the equilibrium degree of swelling, the gels were immersed in solutions at least for one week, during which the solutions were replaced twice. After the swelling equilibrium was established, the diameter of the gels was measured by a calibrated digital compass. The equilibrium swelling ratio of the gels is presented as V/V_w, where V and V_w are the equilibrium volumes of the gel in polymer solution and in water, respectively, which was calculated as

$$V/V_w = (D/D_w)^3 \qquad (1)$$

where D and D_w are the diameter of the gels in polymer solution and in water, respectively. Each swelling ratio reported in this paper is an average of at least four separate measurements; standard deviations of the measured swelling ratios were less than 10% of the mean value.

The concentration of aqueous PEG-300 and PEG-400 solutions used in the swelling experiments ranged from 0 to 100% by volume.

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 0.1 to 0.4 mL of volumes a total amount of 8 mL of water was used for the extraction experiments. For samples of 0.4 to 1 mL of volumes, the amount of water was increased to 20 mL. Each extraction process took one week, during which the solvent was refreshed at least twice until the refractive index of solution becomes equal to that of water. The amount of extracted PEG was measured by refractometry using calibration curves prepared for each PEG sample. A standard deviation of $\mp$ 0.1 was found for the measured PEG distribution between the gel and solution phases.

Results

In Figure 1, the degree of swelling V/V_w of PNIPA gels (filled symbols) and PAAm gels (open symbols) in aqueous PEG-300 solutions is plotted as a function of the PEG volume fraction ϕ in the external solution. The experimental data for PAAm gels were taken from the literature.[15] All the swelling experiments were carried out at 25 °C. The ionic group (AMPS) contents of the networks are shown in the figure. As the PEG volume fraction ϕ in the external solution increases from 0 to 0.60, both gels deswell continuously. In this concentration range of PEG, both gels behave identically. A difference in the swelling behavior of PNIPA and PAAm gels appears if ϕ crosses the value 0.6. PNIPA gels with 0 or 1 mol-% AMPS start to swell again, while PAAm gels continue to deswell in the PEG solutions (Figure 1 A). For higher AMPS contents (Figure 1 B), PNIPA gels remain in the swollen state over the entire range of the external PEG concentration, whereas the PAAm gels collapse discontinuously (for 3 and 6% AMPS) or continuously (for 10% AMPS) and pass to shrunken states in pure PEG.

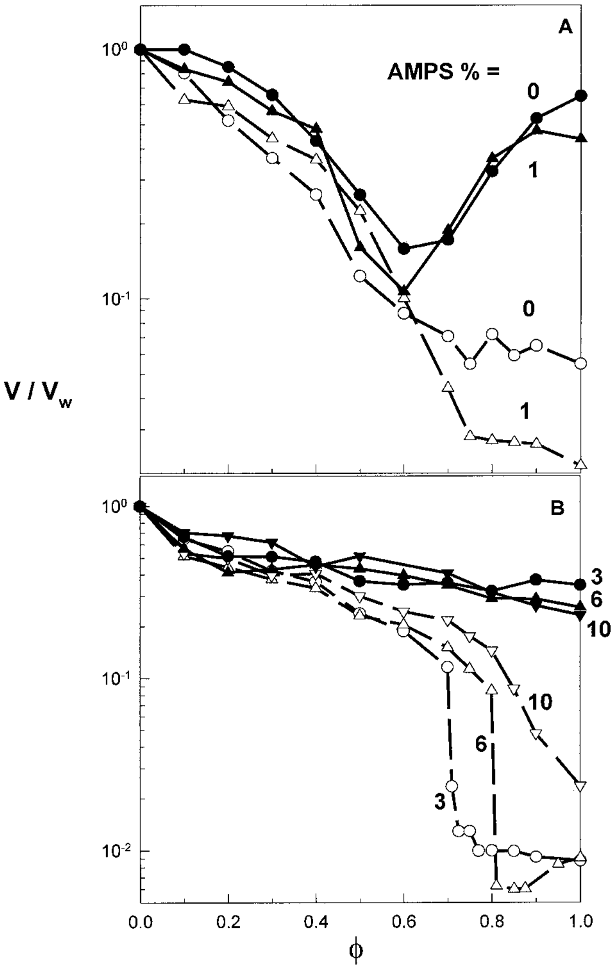

Figure 1. Variation of the swelling ratio V/V_w of PNIPA gels (filled symbols) and PAAm gels (open symbols) with the concentration of PEG-300 in the outer solution. Each PEG concentration is given as volume fraction in the solution phase ϕ. The experimental data for PAAm gels were taken from ref.[15] The ionic group (AMPS) contents of the hydrogels are shown in the figure. The curves show the trend of the data. Swelling temperature = 25 °C.

Since the only difference between the PNIPA and PAAm gels is the existence of isopropyl (IP) groups in PNIPA networks, Figure 1 indicates that the IP groups are responsible for the reentrant transition behavior of PNIPA gels in PEG solutions. As can be seen from Figure 1, the volume of PNIPA gels in PEG melt ($\phi = 1$) is about ten to fifty fold larger than that of PAAm gels of the same ionic group content. This means that the incorporation of IP groups on the network chains creates attractive interactions between the network and PEG segments so that PEG-300 becomes a good polymeric solvent for the PNIPA network at 25 °C. Thus, water and PEG-300 molecules taken separately are good solvents for a PNIPA network. However, in mixtures, since water molecules are hydrogen bonded with the ether oxygen of PEG chains,[23] the attractive water-PEG interactions dominate over the water-PNIPA or PEG-PNIPA interactions. As a result, addition of PEG to water or water to PEG decreases the water content of the gel phase so that the gel contracts and attains a minimum volume at $\phi = 0.6$ (Figure 1 A). For higher ionic group contents (Figure 1 B), the osmotic pressure of counterions inside the gel increases the gel volume so that the PEG chains can easily penetrate into the PNIPA network without an essential loss of their conformational entropy and can interact with water inside the gel phase. As a result, the gel remains in the swollen state over all ϕ values.

In Figure 2, the PEG-300 distribution inside and outside the gel phase (v_3/ϕ) is shown as a function of the PEG-300 concentration in the external solution ϕ. The experimental data are also for 25 °C. The curves in the figure only show the trend of the data. 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.

As expected,[12, 16, 24] the PEG concentration inside the gel is always smaller than that in the solution, i.e., $v_3/\phi <$

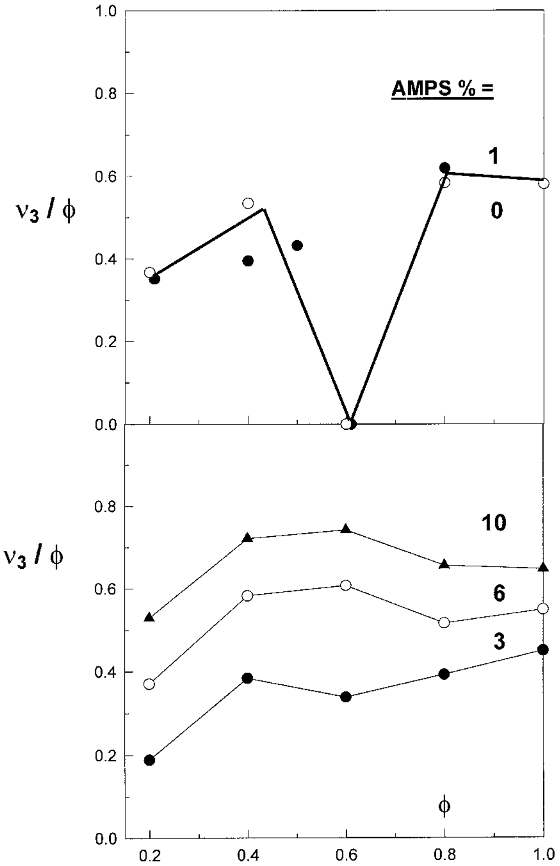

Figure 2. Dependence of the PEG distribution inside and outside the PNIPA gels, ν_3/ϕ, on the PEG-300 concentration in the solution ϕ. The ionic group (AMPS) contents of the hydrogels are shown in the figure. The curves show the trend of the data. Swelling temperature = 25 °C.

1. The accumulation of PEG in the external solution is due to the reduction in the number of arrangements available to the PEG chains penetrating into the gel. The PEG concentration difference between the inside and outside the gel ($\nu_3 - \phi$) creates an osmotic pressure, which contracts the gel in PEG solutions (Figure 1). Furthermore, the ν_3/ϕ ratio increases as the ionic group content of the hydrogels increases. This is a result of increasing gel volume with increasing ionic group content, which facilitates penetration of PEG in the gel. Interestingly, ν_3/ϕ ratios for the PNIPA gels with 0 and 1 mol-% AMPS exhibit minima at $\phi = 0.6$ corresponding to the minima in the swelling curves (Figure 1). Thus, the decrease in the gel volume as ϕ is increased from 0.4 to 0.6 is accompanied by the flow of PEG chains from gel to the solution phase. At $\phi > 0.6$, the direction of the PEG flow changes so that the PEG chains reenter the gel phase causing the gel to swell.

The swelling measurements of PNIPA gels in PEG-300 solutions were also carried out at 18 °C. The results are shown in Figure 3 as filled symbols together with the data obtained at 25 °C (open symbols). Decreasing the swelling temperature from 25 to 18 °C increases the extent of reentrant transition behavior of the gels. In Figure 4, the results of experiments carried out using PEG-400 instead of PEG-300 are shown. The swelling experiments were for 25 °C. Increasing the molecular weight of PEG from 300 to 400 g/mol induces a first-order collapse transition both in non-ionic and ionic PNIPA gels with 1% AMPS at $\phi = 0.55$ and 0.40, respectively while their reswelling at higher ϕ values occurs continuously. PNIPA gels with higher ionic group contents (not shown in the figure) behave similarly to those in PEG-300 solutions (Figure 1 B).

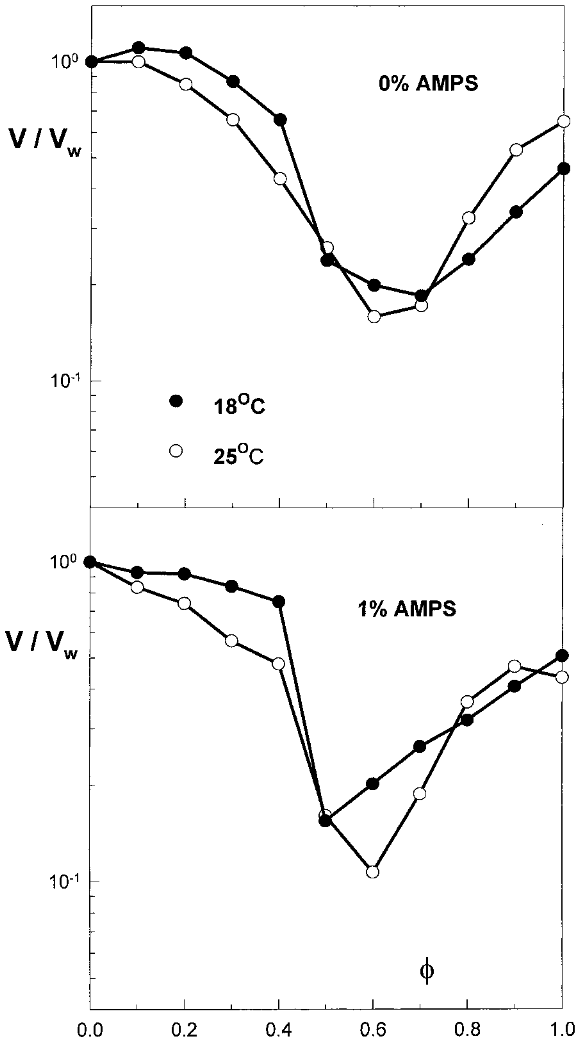

Figure 3. Variation of the swelling ratio V/V_w of PNIPA gels with the concentration of PEG-300 in the outer solution ϕ. The ionic group (AMPS) contents of the hydrogels are shown in the figure. Swelling temperature = 18 (●) and 25 °C (○).

Discussion

In this section, experimental swelling data of PNIPA hydrogels in PEG solutions were analyzed using the FH

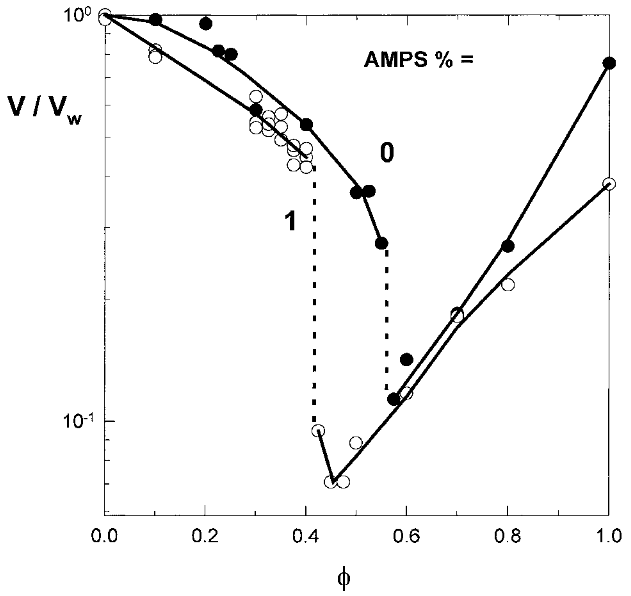

Figure 4. Variation of the swelling ratio V/V_w of PNIPA gels with the concentration of PEG-400 in the outer solution ϕ. The ionic group (AMPS) contents of the hydrogels are shown in the figure. Swelling temperature = 25 °C. The solid curves only show the trend of data. The dotted vertical lines illustrate the phase transition regions.

theory of swelling equilibrium. 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:

$$\Delta G = \Delta G_m + \Delta G_{el} + \Delta G_i \tag{2}$$

According to the FH theory, ΔG_m is given by:[25]

$$\Delta G_m = RT\left(\sum_i n_i \ln v_i + \sum_{i<j} n_i v_j \chi_{ij}\right) \tag{3}$$

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 temperature. For the present (quasi)ternary system, the subscript $i = 1, 2$, and 3 denotes the solvent (water), the network (ionic PNIPA), and the linear polymer (PEG), respectively. For the free energy of elastic deformation ΔG_{el}, although several theories are available, we will use here the simplest affine network model to describe qualitatively the elasticity of PAAm network:[25]

$$\Delta G_{el} = (3/2)V_P\left(\frac{RT}{NV_1}\right)(a^2 - 1 - \ln a) \tag{4}$$

where V_P is the volume of polymer network, N is the average number of segments in the network chains, V_1 is the molar volume of solvent, a is the linear swelling ratio with respect to the after-synthesis- stage of the gel, i.e.,

$$a = \left(\frac{v_2^0}{v_2}\right)^{1/3} \tag{4a}$$

where v_2^0 is the polymer network concentration after the gel preparation. The existence of fixed ions on the network chains results in nonequal distribution of mobile counterions between the inside and outside the gel. For ionic gels, this contribution (ΔG_i) may be written as follows:[25]

$$\Delta G_i = RT f \frac{v_2}{v_1} n_1 \ln(f v_2) \tag{5}$$

where f is the effective charge density of the network, i.e. the fraction of segments bearing ionic groups that are effective in gel swelling. As we have shown recently,[14, 15] the charge density f of the hydrogels in polymer solutions is not a constant but it decreases as the polymer concentration ϕ in the solution increases, i.e. as the dielectric constant of the medium decreases. As a first approximation, the variation of f with the polymer concentration can be written as:[15]

$$f = f_0(1 - A\phi) \tag{5a}$$

where f_0 is the charge density of the network in water and A is the fraction of counterions forming ion pairs in polymer melt.

Substitution of Eq. (3)–(5) into Eq. (2) and differentiating with respect to the number of moles of solvent n_1 and linear polymer n_3 yield the following set of equations for the excess chemical potentials of the solvent and the polymer in both gel ($\Delta\mu_i^{gel}$) and solution phases ($\Delta\mu_i^{sol}$):

$$\frac{\Delta\mu_1^{gel}}{RT} = \ln v_1 + (1 - v_1) - v_3/y + (\chi_{12}v_2 + \chi_{13}v_3)(1 - v_1)$$
$$-\chi_{23}v_2v_3 + N^{-1}(v_2^{1/3}v_2^{0\,2/3} - v_2/2) - v_2 f \tag{6a}$$

$$\frac{\Delta\mu_1^{sol}}{RT} = \ln(1 - \phi) + \phi(1 - 1/y) + \chi_{13}\phi^2 \tag{6b}$$

$$\frac{\Delta\mu_3^{gel}}{yRT} = (1/y)\ln v_3 + (1/y)(1 - v_3) - v_1 + (\chi_{13}v_1 + \chi_{23}v_2)$$
$$(1 - v_3) - \chi_{12}v_1v_2 + N^{-1}(v_2^{1/3}v_2^{0\,2/3} - v_2/2) - v_2 f \tag{7a}$$

$$\frac{\Delta\mu_3^{sol}}{yRT} = (1/y)\ln\phi - (1 - \phi) + (1/y)(1 - \phi)$$
$$+\chi_{13}(1 - \phi)^2 \tag{7b}$$

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:

$$\Delta\mu_1^{\mathrm{gel}} - \Delta\mu_1^{\mathrm{sol}} = 0 \tag{8a}$$

$$\Delta\mu_3^{\mathrm{gel}} - \Delta\mu_3^{\mathrm{sol}} = 0 \tag{8b}$$

Combining Eq. (6) and (8), one obtains the following two equations describing the thermodynamic equilibrium condition of an ionic gel immersed in a polymer solution:

$$\begin{aligned}\ln\left(\frac{1-v_2-v_3}{1-\phi}\right) &+ (v_2+v_3-\phi) - (v_3-\phi)/y + \chi_{12}v_2^2\\ &+\chi_{13}(v_3^2-\phi^2) + (\chi_{12}+\chi_{13}-\chi_{23})v_2v_3\\ &+N^{-1}(v_2^{1/3}v_2^{0\,2/3} - v_2/2) - f v_2 = 0\end{aligned} \tag{9}$$

$$\begin{aligned}-\ln\left(\frac{1-v_2-v_3}{1-\phi}\right) &+ (1/y)\ln(v_3/\phi) - 2\chi_{13}(v_3-\phi)\\ &+(\chi_{23}-\chi_{12}-\chi_{13})v_2 = 0\end{aligned} \tag{10}$$

Eq. (6)–(8) reduce to Eq. (11) and (12) for ionic gels immersed in pure solvent ($v_3 = \phi = 0$) and in polymer melt ($v_1 = 0$), respectively:

$$\begin{aligned}\frac{\Delta\mu_1^{\mathrm{gel}}}{RT} &= \ln(1-v_{2,\mathrm{w}}) + v_{2,\mathrm{w}} + \chi_{12}v_{2,\mathrm{w}}^2 + N^{-1}(v_{2,\mathrm{w}}^{1/3}v_2^{0\,2/3}\\ &- v_{2,\mathrm{w}}/2) - f_0 v_{2,\mathrm{w}} = 0\end{aligned} \tag{11}$$

$$\begin{aligned}\frac{\Delta\mu_3^{\mathrm{gel}}}{yRT} &= (1/y)\ln(1-v_{2,\mathrm{p}}) + v_{2,\mathrm{p}}/y + \chi_{23}v_{2,\mathrm{p}}^2\\ &+N^{-1}(v_{2,\mathrm{p}}^{1/3}v_2^{0\,2/3} - v_{2,\mathrm{p}}/2) - f v_{2,\mathrm{p}} = 0\end{aligned} \tag{12}$$

where $v_{2,\mathrm{w}}$ and $v_{2,\mathrm{p}}$ are the equilibrium volume fractions of polymer network in water and in polymer melt (PEG), respectively.

Eq. (11) and (12) predict the equilibrium volume of the hydrogels in solvent and in polymer melt, respectively. Moreover, simultaneous solution of Eq. (9) and (10) predicts the equilibrium volume of the hydrogels in polymer solutions ($V/V_\mathrm{w} = v_{2,\mathrm{w}}/v_2$) as well as the concentration of the linear polymer molecules in the gel phase (v_3). For the solution of the thermodynamic equations for the present (quasi)ternary system (PNIPA/PEG/water), one needs to know the values of the system specific parameters ϕ, y, v_2^0, N, f_0, A, and χ_{ij} which were derived as follows:

1) Concentration ϕ and the chain length y of PEG in the external solution: ϕ is the independent variable of the present study. y relates to the molecular weight of PEG,[15] i.e. equals 14.7 for PEG-300.
2) The network concentration after the gel preparation v_2^0: v_2^0 was calculated from the initial monomer concentration (8 g/100 mL) together with the polymer density as 0.06. For this calculation, we assumed that the polymer density is equal to the density of PAAm, which is 1.35 g/mL.[26]
3) The interaction parameter between PNIPA and water χ_{12}: The χ_{12} parameter was recently evaluated from the swelling data for non-ionic PNIPA gels swollen in water.[27] Its value at 25 °C is given as

$$\chi_{12} = 0.3875 + 0.518\,v_2 \tag{13}$$

4) The crosslink density (N^{-1}) of the PNIPA gels: The value $v_{2,\mathrm{w}} = 0.042$ found by experiments for the non-ionic PNIPA gels ($f = 0$) swollen in water at 25 °C together with Eq. (11) and (13) gives $N = 172$. This value of N should be valid for all other ionic PNIPA hydrogels because the crosslinker ratio (BAAm/monomers mole ratio) and the total monomer concentration were fixed.
5) The effective charge density f_0 of the hydrogels in water: Substitution of the experimental swelling data of ionic PNIPA gels in water ($v_{2,\mathrm{w}}$) into Eq. (11) leads to their effective charge densities f_0. The values found were $10^2 f_0 = 0.59$, 1.3, 2.3, and 3.3 for hydrogels with 1, 3, 6, and 10 mol-% AMPS, respectively. As expected,[15] f_0 values are about two to three fold smaller than the mole fractions of AMPS used in the gel synthesis. These results are in agreement with those obtained previously for PAAm networks and originate from the existence of osmotically passive counterions inside the gel, and/or due to the finite extensibility of the network chains.[15]
6) The interaction parameter between PNIPA and PEG-300 χ_{23}: Eq. (12) in conjunction with the swelling data of non-ionic PNIPA gels in pure PEG-300 ($v_{2,\mathrm{p}}$) was used to calculate the network-polymer interaction parameter χ_{23}. The value $v_{2,\mathrm{p}} = 0.071$ found by experiments gives $\chi_{23} = 0.0035$. Note that the values χ_{12} and χ_{23} do not depend on the ionic group contents of the hydrogels because the ionic group effect is included in the last term of the swelling equations.[15]
7) Ion pairing coefficient A of the networks: Solution of Eq. (12) together with the experimental swelling data of ionic PNIPA gels in pure PEG-300 gives the coefficient A as 0.68 ± 0.01 indicating that about 70% of counterions in the gel form ion pairs in polymer melt.
8) The interaction parameter between water and PEG-300 χ_{13}. Solution of Eq. (9) and (10) using the reported value for $\chi_{13} = 0.45$[28] gives an initial gel swelling on

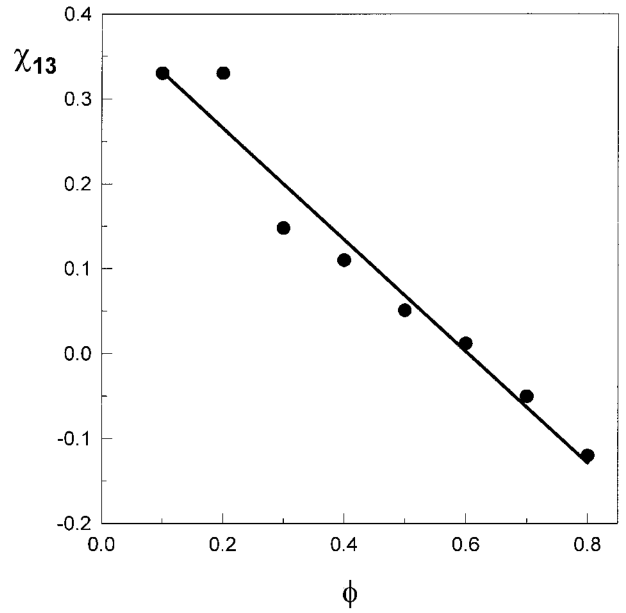

Figure 5. The interaction parameter between water and PEG-300 χ_{13} shown as a function of the PEG concentration ϕ. The line in the figure is a linear best fit to the data points.

rising the external PEG concentration which was not observed experimentally. Moreover, substitution of the recently evaluated value[15] of $\chi_{13} = 0.31-0.21\phi + 0.11\phi^2$ into the swelling equations also provided only poor agreement with the experimental data. Therefore, Eq. (9) and (10) were solved for χ_{13} as a function of ϕ in order to reproduce the experimental swelling data of non-ionic gels in PEG-300 solutions. The calculated values of χ_{13} are shown in Figure 5 plotted as a function of the PEG-300 volume fraction in the solution. The solid line in the figure is a linear best fit to the data points which gives:

$$\chi_{13} = 0.40 - 0.66\,\phi \tag{14}$$

In Table 1, the parameters thus evaluated for the system PNIPA/PEG-300/water at 25 °C are collected. These parameters together with Eq. (9) and (10) can be used to calculate the volume of the hydrogels (V/V_w) as well as the PEG concentration in the gel (v_3) as a function of the volume fraction of PEG in the outer solution ϕ as an independent parameter.

Table 1. The network and interaction parameters for the system ionic PNIPA/PEG-300/water at 25 °C.

$y = 14.7$
$v_2^0 = 0.06$
$N = 172$
$A = 0.68$
$\chi_{12} = 0.3875 + 0.518\,v_2$
$\chi_{23} = 0.0035$
$\chi_{13} = 0.40-0.66\phi$
$10^2 f_0 = 0.59$, 1.3, 2.3, and 3.3 for 1, 3, 6, and 10 mol-% AMPS, respectively.

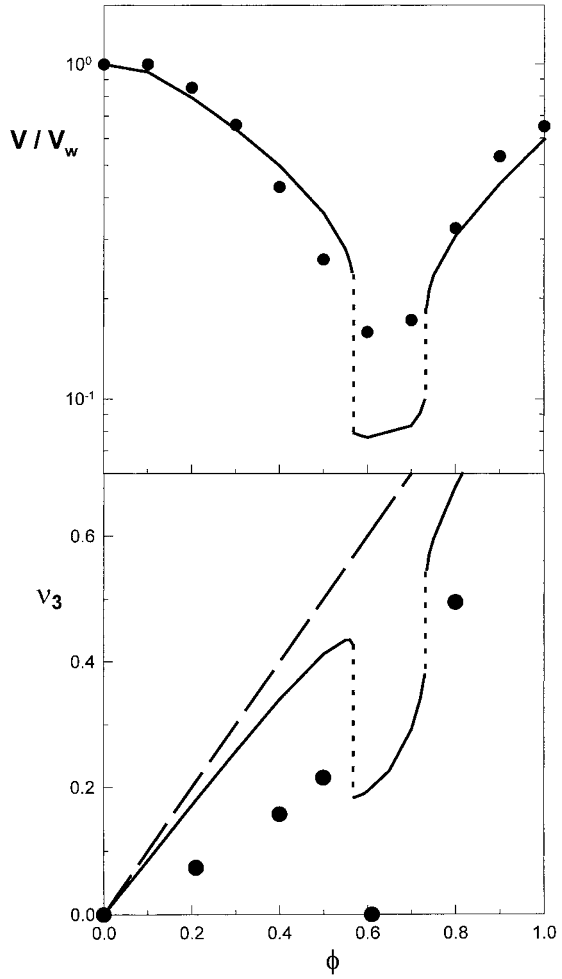

Figure 6. Variations of the swelling ratio V/V_w of non-ionic PNIPA gel and the PEG concentration in gel v_3, with the PEG-300 concentration in the outer solution ϕ. The data points are shown as symbols. The solid curves were calculated using the FH theory. The dashed line represents the relation $v_3/\phi = 1$. The dotted vertical lines illustrate the phase transition regions.

The calculation results are first given in Figure 6 for non-ionic PNIPA gels swollen in PEG-300 solution. Here, the solid curves show the predictions of the theory and the symbols represent the experimental data. The dotted vertical lines represent the phase transition regions. It is seen that the theory is in good agreement with the experimental swelling data, except for the collapsed region, i.e. between $\phi = 0.6$ and 0.7. In this region, the theory predicts sharp first-order collapse and decollapse transitions at $\phi = 0.565$ and 0.735, respectively, compared to the smooth transitions observed by experiments. Reanalysis of Eq. (9) and (10) using the parameters listed in Table 1 indicated a considerable sensitivity of the gel volume to the χ_{13} parameter value in the collapsed region. For example, the curves in Figure 7 showing the variations of V/V_w and v_3/ϕ with the PEG concentration ϕ were calculated using χ_{13} = 0, 0.05, and 0.10. Depending on a slight change in the χ_{13} value, the behavior of reentrant phase transition drastically changes; χ_{13} =

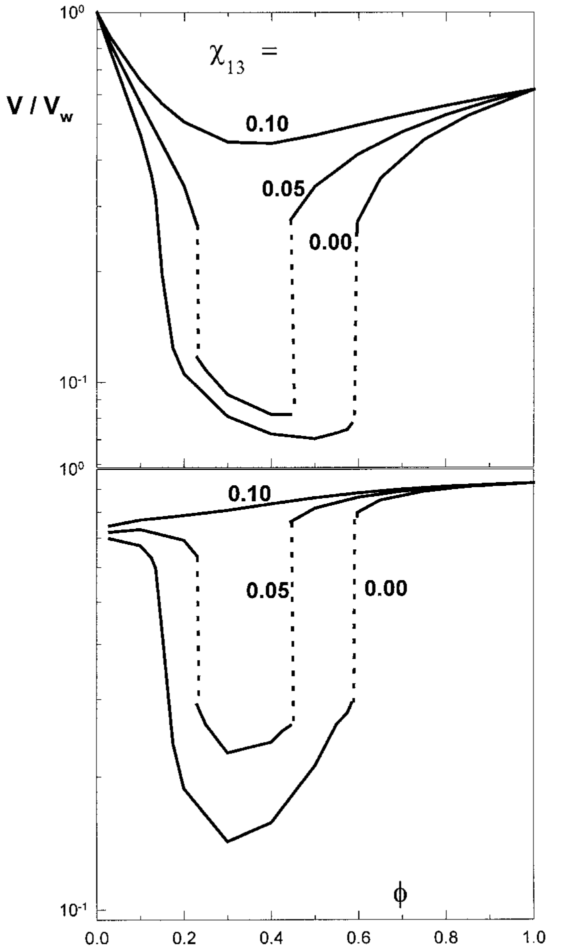

Figure 7. Variations of the swelling ratio (V/V_w) and the PEG distribution inside and outside the non-ionic PNIPA gels (ν_3/ϕ) with the concentration of PEG-300 in the outer solution ϕ. Calculations were using the FH theory with the χ_{13} parameter shown in the figure.

0.10 gives a smooth reentrant transition, whereas χ_{13} = 0.05 predicts first-order collapse and decollapse transitions. For χ_{13} = 0, one obtains a continuous deswelling of the gel followed by a first-order swelling transition.

For the present system, χ_{13} is not a constant but decreases starting from 0.40 as the PEG concentration ϕ increases. According to Eq. (15) and Figure 5, χ_{13} approaches zero at $\phi \cong 0.6$, which induces the reentrant phenomenon in PNIPA gels. Thus, $\chi_{13} \cong 0$ at $\phi \cong 0.6$ is responsible for the reentrant transition behavior of PNIPA gels in PEG solutions. The type of the reentrant transition subtley depends on the exact value of χ_{13}. Figure 6 also indicates only a qualitative agreement between the theoretical and experimental PEG distribution curves. This is believed to be due to the approximations used in the derivation of the FH theory.[8]

In Figure 8, the swelling ratio of the gels V/V_w as well as the PEG concentration in the gel ν_3 calculated using the FH theory are shown as a function of the PEG concentration ϕ for various network charge densities. In agreement with the experiments, reentrant phase transition in the hydrogels appears at low ionic group contents while the gels remain in the swollen state at higher ionic group contents. Although the agreement between the theory and experimental is only qualitative, the present calculations show the condition of reentrant phase transition in gels immersed in polymer solutions. The required values of the parameters are $\chi_{13} \cong \chi_{23} \cong 0, f \cong 0$ and $\chi_{12} \geq 0.4$. Moreover, concentration dependent χ_{12} parameter, such as that of PNIPA-water system, increases the extent of reentrant collapse and decollapse transitions.

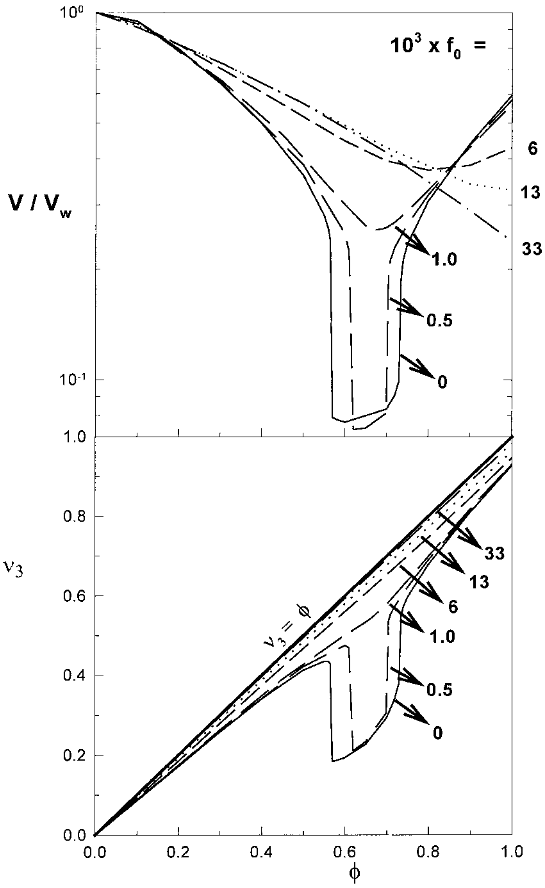

Figure 8. Variations of the swelling ratio (V/V_w) and the PEG concentration inside the PNIPA gels (ν_3) with the concentration of PEG-300 in the outer solution ϕ. Calculations were using the FH theory for a series of values of f_0, which is proportional to the amount of ionizable group incorporated into the network.

Conclusions

In this study, the swelling behavior of strong polyelectrolyte hydrogels based on *N*-isopropylacrylamide (NIPA) and 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) was investigated in aqueous solutions of poly(ethylene glycol)s (PEG) of molecular weights 300 and 400 g/mol. Non-ionic hydrogels or hydrogels with

1 mol-% AMPS show reentrant transitions in PEG-300 and PEG-400 solutions. The transitions from the swollen to collapsed states and then again to the swollen state occur smoothly or jumpwise first-order depending on the external parameters. Calculations indicate attractive interactions between PEG and PNIPA segments, which are responsible for the observed reentrant transition behavior. It was shown that the required condition of reentrant phase transition in PNIPA gels is $\chi_{13} \cong \chi_{23} \cong 0$. Concentration dependent χ_{12} parameter of PNIPA-water system increases the extent of reentrant collapse and decollapse transitions of PNIPA gels.

Acknowledgement: Work was supported by *Istanbul Technical University Research Fund*, contract grant number 1054.

Received: April 12, 2000
Revised: August 16, 2000

[1] R. F. Boyer, *J. Chem. Phys.* **1945**, *13*, 363.
[2] I. Sakurada, A. Nakajima, H. Aoki, *J. Polym. Sci.* **1959**, *35*, 507.
[3] G. Hild, D. Froelich, P. Rempp, H. Benoit, *Makromol. Chem.* **1972**, *151*, 59.
[4] W. R. Good, H.-J. Cantow, *Makromol. Chem.* **1979**, *180*, 2605.
[5] J. Bastide, S. Candau, L. Leibler, *Macromolecules* **1981**, *14*, 719.
[6] F. Horkay, M. Zrinyi, *J. Macromol. Sci. B* **1986**, *25*, 307.
[7] A.-M. Hecht, H. B. Stanley, E. Geissler, F. Horkay, M. Zrinyi, *Polymer* **1993**, *34*, 2894.
[8] F. Brochard, *J. Phys.* **1981**, *42*, 505.
[9] B. T. Poh, K. Adachi, T. Kotaka, *Macromolecules* **1987**, *20*, 2563.
[10] K. Adachi, T. Nakamoto, T. Kotaka, *Macromolecules* **1989**, *22*, 3106.
[11] V. V. Vasilevskaya, A. R. Khokhlov, Y. Matsuzawa, K. Yoshikawa, *J. Chem. Phys.* **1995**, *102*, 6595.
[12] N. Kayaman, O. Okay, B. M. Baysal, *Polym. Gels Network* **1997**, *5*, 167.
[13] N. Kayaman, O. Okay, B. M. Baysal, *Polym. Gels Network* **1997**, *5*, 339.
[14] N. Kayaman, O. Okay, B. M. Baysal, *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1313.
[15] D. Melekaslan, O. Okay, *Polymer* **2000**, *41*, 5737.
[16] V. V. Vasilevskaya, A. R. Khokhlov, *Macromolecules* **19**, *25*, 384.
[17] Y. Hirokawa, T. Tanaka, *J. Chem. Phys.* **1984**, *81*, 6379.
[18] S. Katayama, Y. Hirokawa, T. Tanaka, *Macromolecules* **1984**, *17*, 2641.
[19] S. Katayama, A. Ohata, *Macromolecules* **1985**, *18*, 2781.
[20] T. Amiya, Y. Hirokawa, Y. Hirose, Y. Li., T. Tanaka, *J. Chem. Phys.* **1987**, *86*, 2375.
[21] T. Ishidao, M. Akagi, H. Sugimoto, Y. Iwai, Y. Arai, *Macromolecules* **1993**, *26*, 7361.
[22] S. Durmaz, O. Okay, *Polymer* **2000**, *41*, 3693.
[23] A. Kyritsis, P. Pissis, *J. Polym. Sc., Part B: Polym. Phys.* **1997**, *35*, 1545.
[24] A. R. Khokhlov, S. Starodubtzev, V. V. Vasilevskaya, *Adv. Polym. Sci.* **1993**, *109*, 123.
[25] P. J. Flory, "*Principles of Polymer Chemistry",* Cornell University Press, Ithaca, NY 1953.
[26] M. Ilavsky, *Macromolecules* **1982**, *15*, 782.
[27] S. Hirotsu, *Adv. Polym. Sci.* **1993**, *110*, 1.
[28] J. Brandrup, E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, 1975, page IV-133.