Reentrant Phase Transition of Poly(N-isopropylacrylamide) Gels in Polymer Solutions: Thermodynamic Analysis

NERMIN GÜNDOGAN, OGUZ OKAY
Istanbul Technical University, Department of Chemistry, 80626 Maslak, Istanbul, Turkey

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ABSTRACT: The swelling behavior of poly(N-isopropylacrylamide) (PNIPA) gels in polymer solutions, particularly in aqueous solutions of poly(ethylene glycol)s, was investigated using the theory of equilibrium swelling. The volume of the PNIPA gel and the partition parameter of the macromolecules between the gel and the solution phases were calculated for various extents of the energetic interactions between the components. The simulation results were compared with the experimental data reported in the literature. It was shown that the PNIPA gel has a tendency to a reentrant phase transition in an aqueous solution of low molecular weight linear polymers. In such a transition, the gel first collapses, then reswells, if the linear polymer concentration is continuously varied. The necessary condition for the reentrant behavior of PNIPA gels was predicted in terms of the interaction parameters among the PNIPA network, the linear polymer, and water. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 801–813, 2002

Key words: hydrogels; swelling; thermodynamics; phase diagrams

INTRODUCTION

Volume-phase transitions in hydrogels have been extensively studied in recent years. Poly(N-isopropylacrylamide) (PNIPA) gel is a well-known temperature-sensitive gel exhibiting a swelling or deswelling transition at its lower critical solution temperature (LCST), approximately 34°C in water, which is slightly above the coil–globule transition temperature of linear PNIPA. Below this temperature, the gel is swollen and it shrinks as the temperature is increased.

The temperature sensitivity of PNIPA gels has attracted much attention in the last years due both to fundamental and technological interests. PNIPA gels have been employed for the separation of a range of materials such as macromolecules, yeasts, and bacteria from aqueous solutions. Concentrating such solutions is important because a wide range of biological materials are produced as very dilute solutions. For example, when a shrunken PNIPA gel is added to a dilute high molecular weight polymer solution, the gel swells and absorbs water and other small molecules while macromolecules such as proteins are not absorbed. After recovering the swollen gel and warming, it shrinks drastically and becomes ready for reuse in the concentration process. In this way, the excluded proteins are recovered in a concentrated solution.

In these separation applications, the partitioning of macromolecules between the gel and solution phases is the key factor determining the separation efficiency of PNIPA gels. Accordingly, there is a considerable interest in predicting how the distribution of the macromolecules between the gel and solution phases and the gel volume will depend on the type and the concentration of...
the macromolecules. Although the swelling behavior of PNIPA gels in low molecular weight solvents or solvent mixtures has been studied repeatedly over the last two decades, only a few studies were concerned with swelling in polymer solutions. Vasilevskaya and Khokhlov studied, theoretically, the conformational changes in polymer networks swollen in polymer solutions. They predicted the possibility of a first-order phase transition in such systems. Ishidao et al. investigated the swelling behavior of PNIPA gels in aqueous glucose and starch solutions. They observed that the gel absorbs low molecular weight glucose, but excludes high molecular weight starch (weight-average molecular weights are 30,000 and 180.2 g/mol, respectively). Huglin and coworkers studied the swelling behavior of PNIPA gel immersed in an aqueous solution of poly(ethylene oxide) (PEO) of two different molecular weights. It was shown that the concentration of high molecular weight PEO occurs to a greater degree than that of the low molecular weight species.

Recently, a phenomenon called reentrant swelling transition was observed in PNIPA gels immersed in aqueous solutions of poly(ethylene glycol)s (PEGs) of molecular weights 200–400 g/mol. In such a transition, the gel first collapses, then reswells, if a particular external parameter such as the linear polymer (PEG) concentration is continuously varied. As a consequence, the linear polymer first flows from the gel to the solution phase but then reenters the gel phase at higher polymer concentrations. Reentrant phase transitions in PNIPA gels were also observed in solvent mixtures such as water–dimethyl sulfoxide, water–methanol, or water–ethanol mixtures.

The present work is a theoretical investigation of the condition of the reentrant phase transition in PNIPA gels immersed in an aqueous solution of linear polymers. For this purpose, we analyzed the (quasi)ternary system consisting of the PNIPA network, linear polymer, and water using the Flory–Huggins (FH) theory of swelling equilibrium. Although the predictions of the FH theory are only qualitative due to the several assumptions and approximations used in its derivation, previous works indicate that the theory works successfully to estimate the general swelling features of hydrogels in solutions. This is probably due to favorable cancellation between the approximations of the theory. As will be shown below, general results were obtained illustrating the effects of various parameters such as the energetic interactions between the components on the volume of PNIPA gels in polymer solutions and on the partitioning of the linear polymers between the gel and the external solution. The simulation results were also compared with the experimental data reported in the literature.

**THEORY**

Swelling of a polymer network is governed by at least three free-energy terms, that is, the changes in the free-energy of mixing \( \Delta G_m \), in the free energy of elastic deformation \( \Delta G_{el} \), and in the free energy of electrostatic interactions \( \Delta G_i \):

\[
\Delta G = \Delta G_m + \Delta G_{el} + \Delta G_i
\]

According to the FH theory, \( \Delta G_m \) is given by:

\[
\Delta G_m = RT \left( \sum_i n_i \ln \nu_i + \sum_{i<j} n_i n_j \chi_{ij} \right)
\]

where \( n_i \) is the moles of the species \( i \); \( \nu_i \), its volume fraction; \( \chi_{ij} \), the interaction parameter between the species \( i \) and \( j \); \( R \), the gas constant; and \( T \), the temperature. For the present (quasi)ternary system, the subscript \( i = 1, 2, \) and \( 3 \) denotes water, the PNIPA network, and the linear polymer, respectively (We assume a monodisperse linear polymer.) For the free energy of elastic deformation \( \Delta G_{el} \), although several theories are available, we will use here the simplest affine network model to describe qualitatively the elasticity of the PNIPA network:

\[
\Delta G_{el} = (3/2)V_p \left( \frac{RT}{NV_1} \right) \left( \alpha^2 - 1 - \ln \alpha \right)
\]

where \( V_p \) is the volume of the polymer network; \( N \), the average number of segments in the network chains; \( V_1 \), the molar volume of the solvent; and \( \alpha \), the linear swelling ratio with respect to the after-synthesis-stage of the gel, that is,

\[
\alpha = \left( \frac{\nu_0^2}{\nu_2} \right)^{1/3}
\]

where \( \nu_0^2 \) 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 ($\Delta G_i$) may be written as follows:

$$\Delta G_i = RTf \frac{\nu_2}{\nu_1} n_i \ln(f \nu_2)$$

where $f$ is the effective charge density of the
network, that is, the fraction of segments bearing
ionic groups that is effective in gel swelling. As we
have shown recently, the charge density $f$ of the
hydrogels in polymer solutions is not a constant
but it decreases as the polymer concentration $\phi$ in
the solution increases, that is, as the dielectric
constant of the medium decreases. As a first
approximation, the variation of $f$ with the polymer
concentration can be written as

$$f = f_0 (1 - A \phi)$$

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

Substitution of eqs. (2)–(4) into eq. (1) 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 ($\Delta \mu_i^{sol}$):

$$\frac{\Delta \mu_i^{gel}}{RT} = \ln n_1 + (1 - n_1) - n_3/y$$
$$+ (\chi_{12} \nu_2 + \chi_{13} \nu_3)(1 - n_1) - \chi_{22} \nu_2 \nu_3$$
$$+ N^{-1}(\nu_2^{1/3} \nu_2^{q_{23}} - \nu_2/2) - \nu_2 f$$

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

$$\frac{\Delta \mu_1^{gel}}{yRT} = (1/y) \ln n_1 + (1/y)(1 - n_3) - n_1$$
$$+ (\chi_{12} \nu_1 + \chi_{23} \nu_2)(1 - n_3) - \chi_{12} \nu_1 \nu_2$$
$$+ N^{-1}(\nu_2^{1/3} \nu_2^{q_{23}} - \nu_2/2) - \nu_2 f$$

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

where $y$ is the number of segments in the linear
polymer and $\phi$ is its volume fraction in the solution
phase. The state of equilibrium swelling of a
network immersed in a polymer solution is ob-
tained when the solvent and the polymer inside
the network are in thermodynamic equilibrium
with those outside. This equilibrium state is de-
scribed by the equality of the chemical potential $\mu$
of these components in both phases. Thus, at
swelling equilibrium, we have

$$\Delta \mu_1^{gel} - \Delta \mu_1^{sol} = 0$$
$$\Delta \mu_3^{gel} - \Delta \mu_3^{sol} = 0$$

Combining Eqs. (5) and (7), one obtains the fol-
lowing two equations describing the thermody-
namic equilibrium condition of an ionic gel im-
mersed in a polymer solution:

$$\ln \left( \frac{1 - \nu_2 - \nu_3}{1 - \phi} \right) + (\nu_2 + \nu_3 - \phi) - (\nu_3 - \phi)/y + \chi_{12} \nu_2^2$$
$$+ \chi_{13} \nu_2^2 + (\chi_{12} + \chi_{13} - \chi_{23}) \nu_3 \nu_3$$
$$+ N^{-1}(\nu_2^{1/3} \nu_2^{q_{23}} - \nu_2/2) - f \nu_2 = 0$$

$$-\ln \left( \frac{1 - \nu_2 - \nu_3}{1 - \phi} \right) + (1/y) \ln(\nu_3/\phi) - 2\chi_{13}(\nu_3 - \phi)$$
$$+ (\chi_{23} - \chi_{12} - \chi_{13}) \nu_2 = 0$$

RESULTS AND DISCUSSION

The equilibrium concentrations of water, the
PNIPA network, and the linear polymer in the gel
can be obtained by solving eqs. (8) and (9) for a
given linear polymer concentration $\phi$ of the exter-
nal solution. In the following sections, the calcu-
lation results are presented in terms of the vol-
ume fraction of the components $n_i$ and the linear
polymer partition parameter $\nu_3/\phi$. Note that the
partition parameter $\nu_3/\phi = 1$ means that the poly-
mer concentration in the gel is equal to that in the
solution, while $\nu_3/\phi = 0$ means total exclusion
of the linear polymer molecules from the PNIPA gel.

The parameters in the construction of theoreti-
cal equilibrium swelling and polymer partition
parameter curves were not arbitrarily selected;
they are chosen to be very close to the typical
experimental parameters. PNIPA gels are usu-
ally prepared by free-radical crosslinking copoly-
merization of the N-isopropylacrylamide (NIPA)
monomer with the $N,N'$-methylenebisacrylamide (BAAm) crosslinker in aqueous solutions. The monomer concentration used in the gel preparation is usually 8 g/100 mL solution, which corresponds to $v_0^2 = 0.06$. Furthermore, the mol ratio of the crosslinker BAAm to the monomer NIPA is also fixed by the experiments at 1/82, which gives a chemical crosslink density $N = 41$, if all BAAm molecules form effective crosslinks in the final PNIPA hydrogel. However, using the swelling measurements, the value of $N$ was found to be 172, indicating that a large fraction of BAAm units is wasted due to the cyclization and multiple crosslinking reactions during the gel-formation process.\(^{13}\) In the following calculations, the PNIPA network parameters were fixed at $v_0^2 = 0.06$, $N = 170$. The ion-pairing coefficient $A$ was set to 0.68, which was recently calculated from the swelling data of ionic PNIPA gels in polymer melt.\(^{13}\) The interaction parameter between PNIPA and water $\chi_{12}$ was evaluated from the swelling data for nonionic PNIPA gels in water and it is given as\(^{27}\)

$$\chi_{12} = 3.415 - \frac{902.2}{T} + 0.518v_2 \quad (10)$$

where $T$ is the temperature in Kelvin.

The number of segments in the linear polymer $y$ is an important parameter determining the gel volume and the polymer partitioning in the system. The effect of $y$ on the gel swelling has been dealt with in detail previously.\(^{14,21}\) Our preliminary calculations indicated the appearance of distinct reentrant phase transitions in PNIPA gels if $y$ is set to a relatively small value. For example, Figure 1 shows how the equilibrium volume fraction of the crosslinked polymer in the gel $v_2$ varies with the linear polymer concentration $\phi$ in the external solution. Calculations were for different values of $y$ indicated in the figure. Note that, in addition to the polymer volume fraction $v_2$, the experimental swelling data in the literature are also reported in terms of $q_y$ and $V/V_0$, which are the volume swelling ratios with respect to the dry state and to the state after the gel preparation, respectively. These quantities are related to each other using the equations $q_y = 1/v_2$ and $V/V_0 = v_2^0/v_2$. Figure 1 shows that, for a given linear polymer concentration $\phi$, the gel deswells, that is, $v_2$ increases as the number of segments in the linear polymer $y$ increases; the gel collapses at sufficiently large values of $y$. The first-order col-

![Figure 1](image)

**Figure 1** Volume fraction of crosslinked polymer in the gel $v_2$ shown as a function of the polymer concentration $\phi$ in the external solution. $T = 298$ K; $\chi_{13} = 0$; $\chi_{23} = 0.05$. The values of $y$ used in the calculations are indicated in the figure. The dotted lines represent the phase-transition regions.

**Effect of Linear Polymer–Water Interactions**

The effect of the extent of the linear polymer–water interactions represented by $\chi_{13}$ on the uncharged PNIPA gel swelling and the polymer partition parameter $v_2/\phi$ was investigated at $T = 298$ K and $\chi_{23} = 0$. As pointed out in the previous section, calculations were for $y = 14.7$, which corresponds to the number of segments in PEG of molecular weight 300 g/mol (PEG-300). The phase diagram in Figure 2 shows how the PNIPA gel composition varies with $\chi_{13}$. The gel composition is represented by $v_i$, where the subscript $i = 1, 2, 3$ denotes the volume fractions of water, PNIPA, and the linear polymer, respec-
Each apex of the triangle corresponds to the pure component $i$. For example, the $v_1-v_2$ side of the triangle corresponds to mixtures of water and PNIPA network, while the $v_2-v_3$ side corresponds to mixtures of the PNIPA network and the linear polymer. The loci of the solution of eqs. (8) and (9) are drawn in the solid curves in Figure 2. For certain values of $\chi_{13}$, eqs. (8) and (9) were satisfied by three values of both $v_2$ and $v_3$, indicating the coexistence of two gel phases with different conformations and the appearance of a van der Waals loop in the swelling curves. In these cases, the composition of the gels in coexisting phases was calculated by equating the chemical potentials of the network chains in both gel phases. These phase-transition regions are represented in Figure 2 by the dotted curves.

Calculations were for different volume fractions of the linear polymer in the external solution $\phi$, which were varied between 0 and 1. $\phi$ increases from 0 to 1 as one moves along the composition curve from the $v_1-v_2$ to the $v_2-v_3$ sides of the triangle. Depending on the value of $\chi_{13}$, the swelling behavior of PNIPA gels in a polymer solution changes drastically:

For $\chi_{13} \gg 0$ (curves 9 and 10 in Fig. 2), that is, for repulsive interactions between the linear polymer and water, $v_2$ does not change much with the linear polymer concentration in the solution $\phi$, but $v_3$ monotonically increases with increasing $\phi$ from 0 to 1. Thus, the gel remains in the swollen state over the entire range of $\phi$, while the solution inside the gel is enriched by the linear polymer, as $\phi$ is increased. This prediction is physically due to the attractive interactions between the segments of the linear polymer and PNIPA ($\chi_{23} \ll 0$) compared to the repulsive interactions between the linear polymer and water ($\chi_{13} \gg 0$), which facilitates penetration of linear chains into the PNIPA gel. Although the conformational entropy of linear chains penetrating into the gel decreases due to the reduction in the number of their arrangements, the energy gain due to the contact between the linear polymer and PNIPA segments exceeds the decrease in the conformational entropy, so that the chains easily penetrate into the gel. The higher the polymer concentration in the outer solution, the greater its penetration into the hydrogel (Fig. 2). As a consequence, the partition parameter attains values close to 1 over all $\phi$. 

Figure 2  Phase diagram for the ternary system PNIPA network–linear polymer–water at 298 K. $\chi_{23} = 0$, $\chi_{13} = (1) -0.15$, (2) -0.05, (3) 0, (4) 0.03, (5) 0.05, (6) 0.06, (7) 0.063, (8) 0.10, (9) 0.45, and (10) 0.60. Calculations were for $\gamma = 14.7$, which corresponds to the number of segments in PEG of molecular weight 300 g/mol (PEG-300).
values, that is, the composition of the polymer solution in the gel is close to that in the outer solution, which keeps the gel volume almost constant in polymer solutions.

For small or negative values of $\chi_{13}$ (attractive interactions between the linear polymer and water), the gel exhibits reentrant conformational transitions (curves 1–8 in Fig. 2). These transitions are also illustrated in Figures 3 and 4 as the dependencies of the polymer partition parameter $v_2/\phi$ (the linear polymer concentration in the gel divided by that in the external solution) and $v_3$ on the polymer concentration $\phi$ for different values of the $\chi_{13}$ parameter. At low concentrations of the linear polymer $\phi$, the partition parameter $v_2/\phi$ is a decreasing function of $\phi$ while $v_2$ rapidly increases. Thus, in dilute polymer solutions, the fraction of linear polymer chains penetrating into the hydrogel network decreases and the gel deswells as the polymer concentration $\phi$ in the external solution increases. However, the opposite behavior is observed at high polymer concentrations. In this regime, $v_2$ rapidly decreases with increasing $\phi$, that is, the gel starts to swell again as the polymer concentration increases and the linear polymer reenters the gel phase. In polymer melt ($\phi = 1$), the PNIPA gel is swollen and the partition parameter is close to unity.

Figure 4 also shows that both the deswelling and reswelling transitions in PNIPA gel take place in a narrow range of polymer concentration, inside which the gel is in a collapsed state. Depending on a slight change in $\chi_{13}$, the behavior of the reentrant transition drastically changes (Figs. 2–4). For example, $\chi_{13} \simeq 0.063$ gives a smooth reentrant transition, whereas $0.063 > \chi_{13} > 0.03$ predicts first-order collapse and decollapse transitions. For $0.03 > \chi_{13} > -0.11$, one obtains a continuous deswelling of the gel followed by a first-order swelling transition. The phase transition regions in Figures 2–4 are shown as dotted lines. The ends of these lines give the composition of the coexisting gel phases at a particular $\chi_{13}$ value. Combination of these end points at various $\chi_{13}$ values build a closed-loop phase boundary, which represents a domain of instability (Fig. 4). Inside this closed domain, the PNIPA gel must separate into two phases, each having different gel volume and linear polymer concentration. Points A and B shown in Figure 4 on the phase boundary correspond to the lower and upper critical points, respectively, that is, if $\phi < A$ or $\phi > B$, only one gel phase exists, but for $A < \phi < B$, two gel phases may coexist depending on the value of $\chi_{13}$.

Figure 3  Polymer partition parameter $v_2/\phi$ shown as a function of the polymer concentration $\phi$ in the external solution. $T = 298$ K; $y = 14.7$; $\chi_{23} = 0$. $\chi_{13}$ = (1) $-0.15$, (2) $-0.05$, (3) 0, (4) 0.03, (5) 0.05, (6) 0.06, (7) 0.063, (8) 0.10, (9) 0.25, (10) 0.45, and (11) 0.60.
The reentrant swelling behavior of PNIPA gels in polymer solutions predicted for small values of $\chi_{13}$ is due to the competition of two attractive interactions. A linear polymer is attracted both by water ($\chi_{13} < 0$) and by the PNIPA hydrogel ($\chi_{23} = 0$). At low polymer concentrations, polymer–water interactions dominate over polymer–PNIPA interactions, so that the polymer mainly remains in the solution phase. As a consequence, the solution phase is more concentrated than is the gel phase, which results in an osmotic pressure that deswells the gel. However, at a high polymer concentration, polymer–PNIPA attractions dominate over the polymer–water interactions due to the increasing number of contacts between the segments of the linear polymer and PNIPA, so that linear polymer chains again penetrate into the gel and result in the gel swelling.

The results reveal that the PNIPA gel at 298 K should exhibit a reentrant phase transition, if the following conditions are satisfied: $\chi_{13} \equiv 0$, $\chi_{23} = 0$. Thus, a reentrant transition requires two competing forces attracting the linear polymer molecules. Polymer molecules flow from the gel to the solution phase or vice versa depending on their concentration in the external solution.

To test the validity of the theoretical predictions, experimental swelling data of PNIPA gels in polymer solutions reported in the literature are collected in Figure 5 as filled symbols plotted as a function of $\phi$. PEG of molecular weights 300 g/mol (PEG-300) corresponding to $y = 14.7$ was used as the linear polymer in the swelling experiments. For comparison, the swelling data of polyacrylamide (PAAm) gels in PEG-300 are also shown in the figure as open symbols. It is seen that the PNIPA gel exhibits reentrant phase transition in PEG solutions, while PAAm gel continuously deswells as the PEG concentration $\phi$ is increased. PEG is known to be attracted by water.
through the hydrogen-bonding interactions between water and the ether oxygen of PEG chains. PEG is also attracted by the PNIPA gel due to the hydrophobic interactions between the isopropyl groups of PNIPA and the ethylene groups of PEG. Thus, the competing interactions between PEG–water and PEG–PNIPA result in the reentrant swelling behavior of the PNIPA gel shown in Figure 5. However, the collapsed state of the PAAm gel in the PEG melt shown in the figure at $\phi = 1$ indicates that the segments of PAAm and PEG repel each other. As a result, the PAAm gel does not show reentrant behavior due to the repulsive interactions between the PEG and PAAm segments.

**Effect of Temperature**

Although many experimental studies have dealt with the effect of temperature on the swelling behavior of PNIPA gels in low molecular weight solvents, no work can be found in the literature showing how the volume of the gels in polymer solutions and the polymer partition parameter vary with the temperature. Figure 6 shows a phase diagram of PNIPA gels in polymer solu-

![Figure 5](image_url)

**Figure 5** Volume fraction of crosslinked polymer in the gel $v_2$ shown as a function of PEG-300 concentration $\phi$ in the external solution, $T = 298$ K. Experimental data were taken from the literature. The curves only show the trend of the data.

![Figure 6](image_url)

**Figure 6** Phase diagram for the ternary system PNIPA network–linear polymer–water at various temperatures. $\chi_{13} = \chi_{23} = 0$; $y = 14.7$. Temperatures in °C are indicated in the figure.
tions of various temperatures. In Figure 7, the partition parameter $\nu_3/\phi$ and the crosslinked polymer volume fraction in the gel $\nu_2$ are plotted as functions of $\phi$ for various temperatures. Calculations were for $x_{13} = x_{23} = 0$ and $y = 14.7$. It is seen that the contribution of temperature to the shape of the swelling and partition parameter curves is significant. Depending on the temperature, three different regimes can be identified from the figures:

1. If the temperature $T$ is much lower than the LCST of PNIPA, the gel is in a swollen state over the entire range of polymer concentration $\phi$ so that the polymer molecules can easily penetrate the PNIPA gel, that is, the partition parameter is close to unity.

2. At temperatures above the LCST of PNIPA, the gel is in a collapsed state up to a critical polymer concentration, above which the gel undergoes a swelling transition in a narrow range of polymer concentration (Fig. 7). Moreover, the partition parameter $\nu_3/\phi$ is close to zero for the collapsed PNIPA, that is, the linear polymer is not absorbed by the gel below the critical polymer concentrations, above which—simultaneously with the swelling transition—$\nu_3$ rapidly increases and approaches the value of $\phi$, that is, the partition parameter approaches unity. The polymer concentration required for the swelling transition shifts to smaller values as the temperature decreases.

3. Another very remarkable change in the swelling behavior of PNIPA gel appears at temperatures slightly below the LCST of PNIPA. Here, the gel exhibits a reentrant phase transition, in which the gel first deswells, then reswells, if the polymer concentration is monotonically increased.

When a PNIPA network is immersed into water, two phenomena are simultaneously observed: One is hydrophobic hydration, in which the water molecules form ordered cagelike structures around the PNIPA network chains. The other is hydrophobic interaction or association of hydrophobic isopropyl (IP) groups. Below the LCST of PNIPA, the gel is swollen in water because the hydration effect of water molecules dominates over the association forces between the IP groups. However, if polymer chains are introduced into water, the osmotic pressure due to the concentration difference of polymer chains between the inside and outside of the gel compresses the PNIPA gel and strengthens the association forces between IP groups. This compressing effect of linear chains becomes dominant at temperatures slightly below the LCST of PNIPA. As a result, the gel deswells as the polymer concentration increases.

Furthermore, if the temperature exceeds the LCST of PNIPA, water molecules surrounding the network chains start to dissociate so that the hydrophobic interaction dominates over the hydrophobic hydration. As a result, the gel collapses in water. According to Figure 7, the linear poly-

![Figure 7](image_url)
mer chains cannot enter into the collapsed PNIPA gel. This is because the conformational entropy of a single chain in the solution is much higher than that in the collapsed gel. As a result, the linear polymer accumulates in the solution and compresses the PNIPA gel further. The swelling transition of the gel observed above a critical polymer concentration indicates that the favorable linear polymer–PNIPA interactions, represented by $\chi_{23} = 0$, compensate more than do the large losses in the entropy of the linear polymer molecules entering the gel. Thus, in concentrated polymer solutions, the linear polymer penetrates into the gel and results in gel swelling.

Figures 6 and 7 also show that, in a certain range of temperature, the swelling and deswelling transitions occur first-order jumpwise. An island of instability is seen in Figure 7, in which the gel separates into two phases. Figure 8(A,B) show the swelling curves of PNIPA gels for various temperatures calculated for $\chi_{13} = 0.1$ and $0.2$, respectively. Comparison of Figures 7 and 8 shows that the closed domain of instability shifts to higher temperatures as the $\chi_{13}$ parameter increases. Thus, as the quality of the solvent (water) for the linear polymer becomes worse, the temperature required for the reentrant behavior also increases. These results reveal that, for a linear polymer–water system with a positive $\chi_{13}$ parameter value, a reentrant phase transition in the PNIPA gel can be induced by increasing the temperature. Using eq. (10), the following condition was calculated for the reentrant phenomena: $\chi_{23} = 0$ and $\chi_{12} \approx \chi_{13} + 0.5$.

Effect of the Linear Polymer–PNIPA Interactions

Figures 9 and 10 show the dependencies of $\nu_2/\phi$ and $\nu_2$ on the polymer concentration $\phi$ for different values of the linear polymer–PNIPA interaction parameter $\chi_{23}$. Calculations were for $\chi_{13} = 0$ and $0.1$ in Figures 9 and 10, respectively. $y$ was also fixed at 14.7.

If $\chi_{23} \ll \chi_{13}$, that is, if the attractive interactions between the linear polymer and PNIPA are stronger than are those between the linear polymer and water, the linear polymer can penetrate into the gel and results in the swelling of the hydrogel over all the range of $\phi$. As $\chi_{23}$ increases and approaches $\chi_{13}$, the forces acting on the linear polymer from the gel and from the outer solution become equal in magnitude. The appearance of two competing forces in the system results in the reentrant transition of the PNIPA gel. The higher the $\chi_{13}$ parameter, the higher is the $\chi_{23}$ parameter required for the reentrant behavior. On the other hand, if $\chi_{23} \gg \chi_{13}$, that is, if the linear polymer is incompatible with PNIPA, the linear polymer remains mainly in the solution phase so that the resulting concentration difference between the solution and gel phases leads to the deswelling of the gel. In this case, the amount of the linear polymer excluded from the gel increases and the gel volume decreases monotonically as the external polymer concentration increases.

Figure 8: Volume fraction of crosslinked polymer in gel $\nu_2$ shown as a function of the polymer concentration $\phi$ in the external solution. $y = 14.7; \chi_{23} = 0, \chi_{13} = (A) 0.1$ and (B) 0.2. The temperatures in °C are indicated in the figure.
Effect of the Charge Density of PNIPA Gel

Introduction of ionic groups into the hydrogels is known to increase their volume in water. This is due mainly to the simultaneous increase of the mobile counterion concentration inside the gel because of the condition of electroneutrality. The concentration difference of mobile ions between the inside and the outside the gel creates an additional osmotic pressure that swells the gel. Figures 11 and 12 show the effect of the charge density $f$ on the swelling behavior of the PNIPA gel, in terms of $v_2$, and on the partition parameter of linear polymer $v_3/\phi$. Calculations were for $\chi_{13} = 0$ and 0.05, respectively. It is seen that, even at very small charge densities, the gel remains in the swollen state over all $\phi$ values, indicating that the osmotic pressure of mobile counterions dominates over the energetic interactions between the components. Due to the large volume of the ionic PNIPA gels, the polymer chains can easily penetrate into the network without an essential loss of their conformational entropy so that the partition parameter is close to unity. Figures 11 and 12 also

**Figure 9** Polymer partition parameter $v_3/\phi$ and volume fraction of crosslinked polymer in gel $v_2$ shown as a function of the polymer concentration $\phi$ in the external solution. $\chi_{13} = 0; T = 298 K; y = 14.7$. $\chi_{23} = (1) -0.10, (2) -0.04, (3) -0.025, (4) -0.0175, (5) -0.01, (6) 0, (7) 0.0035, (8) 0.006, (9) 0.01, (10) 0.0125, (11) 0.018, (12) 0.025, (13) 0.05, and (14) 0.20.

**Figure 10** Polymer partition parameter $v_3/\phi$ and volume fraction of crosslinked polymer in gel $v_2$ shown as a function of the polymer concentration $\phi$ in the external solution. $\chi_{13} = 0.1; T = 298 K; y = 14.7$. $\chi_{23} = (1) -0.20, (2) 0, (3) 0.006, (4) 0.0125, (5) 0.015, (6) 0.018, (7) 0.025, (8) 0.03, (9) 0.04, (10) 0.08, and (11) 0.20.
show that the extent of the reentrant phase transition increases as the network charge density decreases.

To test the theoretical predictions, experimental swelling data of PNIPA gels in PEG-300 solutions are collected in Figure 13, plotted as a function of the PEG-300 concentration in the external solution. The solid and open symbols in the figure are the data points for the uncharged PNIPA gel and for the PNIPA gel with a 3 mol% ionic group (2-acrylamido-2-methylpropanesulfonic acid sodium salt, AMPS) content, respectively. In accord with the theory, the gel-bearing ionic groups remain in a swollen state over the entire range of PEG concentrations while the uncharged gel exhibits a reentrant phase transition.

CONCLUSIONS

The swelling behavior of PNIPA gels in polymer solutions was investigated using the theory of equilibrium swelling. The parameters in the calculations were chosen to be very close to the typical experimental parameters. The results show that the uncharged PNIPA gel has a tendency to

Figure 11 Polymer partition parameter $\nu_2/\phi$ and volume fraction of crosslinked polymer in gel $\nu_2$ shown as a function of the polymer concentration $\phi$ in the external solution. $x_{13} = x_{23} = 0; T = 298$ K; $y = 14.7$. $10^2 f_0 = (1) 0$, (2) 0.1, (3) 0.6, (4) 1.3, and (5) 3.3.

Figure 12 Polymer partition parameter $\nu_2/\phi$ and volume fraction of crosslinked polymer in gel $\nu_2$ shown as a function of the polymer concentration $\phi$ in the external solution. $x_{13} = 0.05; x_{23} = 0; T = 298$ K; $y = 14.7$. $10^2 f_0 = (1) 0$, (2) 0.05, (3) 0.1, (4) 0.6, (5) 1.3, and (6) 3.3.
a reentrant phase transition in aqueous solutions of low molecular weight linear polymers, that is, the gel first collapses, then reswells, if the linear polymer concentration is continuously varied.

For repulsive interactions between the linear polymer and water, the gel remains in the swollen state over the entire range of the linear polymer concentration $\phi$, while for attractive interactions between the linear polymer and water, the gel exhibits reentrant conformational transitions. Increasing the temperature of the system, or the increasing compatibility between the segments of the linear polymer and PNIPA, promotes the occurrence of a reentrant phase transition in a PNIPA gel. In terms of the interaction parameters among the PNIPA network, the linear polymer, and water, the necessary condition for the reentrant behavior was calculated as $\chi_{12} \equiv 0$, $\chi_{23} \equiv 0$, and $\chi_{13} \equiv \chi_{12} + 0.5$.

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