Polymer Bulletin 49, 181-188 (2002)

Polymer Bulletin

Temperature dependent swelling behavior of ionic poly(N-isopropylacrylamide) gels in PEG solutions

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Received: 31 May 2002/Revised version: 5 August 2002/ Accepted:5 August 2002

Summary

The swelling behavior of poly(N-isopropylacrylamide) (PNIPA) hydrogels in aqueous solution of poly(ethylene glycol) (PEG) and the partition parameter of PEG between the gel and the external solution were investigated. The molecular weight of PEG, the ionic group content of the hydrogels and the swelling temperature were taken as the independent variables. Several types of volume phase transitions such as swelling, deswelling and reentrant phase transitions were observed depending on the external parameters. The results were explained in terms of the theory of equilibrium swelling.

Introduction

Poly(N-isopropylacrylamide) (PNIPA) gel is a well-known temperature - sensitive gel exhibiting swelling or deswelling transition at about 34°C in water [1]. Such temperature-sensitive hydrogels have been suggested for use in a variety of applications, including separation processes of polymer molecules from aqueous solutions [2,3]. 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 were concerned with swelling in polymer solutions. Vasilevskaya and Khokhlov studied theoretically the conformational changes in polymer networks swollen in polymer solutions [4]. Kayaman et al investigated the swelling behavior of poly(acrylamide) (PAAm) gels immersed in aqueous solutions of linear PAAm's as well as in poly(ethylene glycol)'s (PEG) of various molecular weights [5,6]. It was shown that ionic PAAm gels exhibit a discontinuous volume change upon continuous increase of the PEG concentration in the solution. Recently, a phenomenon called reentrant swelling transition was observed in PNIPA gels immersed in aqueous PEG solutions [7-9]. 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.
In the present work, we investigated the swelling behavior of ionic PNIPA hydrogels

in PEG solutions and the partition parameter of PEG between the gel and the external solution. The swelling temperature, the ionic group (2-acrylamido-2-methylpropane sulfonic acid sodium salt, AMPS) content of the hydrogels and the molecular weight of PEG were taken as the independent parameters. The temperature dependence of the swelling behavior of PNIPA hydrogels in PEG solutions has not been studied before. As will be shown below, several types of volume phase transitions were observed depending on the external parameters.

Experimental

Materials

N-isopropylacrylamide (NIPA, Aldrich) N,N'-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and N,N,N',N'-tetramethylethylenediamine (TEMED) were used as received. 2-acrylamido-2-methylpropane sulfonic acid was crystallized from boiling methanol. It was neutralized with NaOH and a stock solution was prepared containing 0.966 M AMPS. Reagent-grade PEGs of molecular weights 200, 300, 400, and 600 g/mol (PEG – 200, - 300, - 400 and - 600, respectively) were purchased from Fluka, and used without further purifications.

Synthesis of the hydrogels

PNIPA gels were prepared by free-radical crosslinking copolymerization of NIPA and AMPS with a small amount of BAAm in aqueous solution at 5^0C. APS (3.51 mM) and TEMED (0.25 mL/100 mL reaction solution) were used as the redox initiator system. The initial monomer concentration was fixed at 0.70 M throughout this study. The crosslinker ratio *X* (mole ratio of the crosslinker BAAm to the monomers NIPA + AMPS) was also fixed at 1/82, while the AMPS content in the monomer mixture was varied between 0 and 6 mol%. Details of the hydrogel preparation and the characteristic data of the hydrogels, including the volume fraction of crosslinked PNIPA after the gel preparation ν_2^0, and the elastic moduli of the hydrogels were reported elsewhere [11].

Swelling Measurements in PEG solutions

Swelling measurements were carried out at various temperatures in aqueous PEG solutions. The volume fraction of PEG in the aqueous solutions, denoted by ϕ, ranged from 0 to 1. The hydrogel samples in the form of rods of 5 mm in diameter and approximately 10 mm in length 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 gels were immersed in solutions at least for two weeks replacing the solutions every other day. After the swelling equilibrium is established, the diameter of the gels was measured by a calibrated digital compass. To achieve good precision, three measurements were carried out on samples of different length taken from the same gel. The normalized volume of the equilibrium swollen hydrogels V/V_0 (volume of equilibrium swollen gel/volume of the gel just after preparation) was calculated as

$V/V_o = (D/D_o)^3$, where D and D_o are the diameter of hydrogels after equilibrium swelling and after synthesis, respectively.

Absorption Measurements

The PEG concentration inside the gel samples was measured by refractometry using an Abbe refractometer 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. Each extraction process took one week, during which water 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 ∓ 0.1 was found for the measured PEG distribution between the gel and solution phases (ν_3/ϕ).

Results and discussion

Effect of the network charge density

In Figure 1, the swelling ratio V/V_o of PNIPA gels containing varying amounts of AMPS is plotted against the PEG volume fraction in the external solution ϕ. The swelling experiments were carried out at 25^0C and using PEG-300 as the linear polymer. At AMPS contents equal or higher than 3%, the gels remain in the swollen state ($V/V_o > 1$) over all ϕ ranges, indicating that the osmotic pressure of mobile counterions (Na^+) in the gel determines the swelling process of highly charged PNIPA gels in polymer solutions. However, if the AMPS content of the hydrogels is less than 3%, the gels undergo reentrant conformational transitions, in which they first deswell, then reswell if the PEG concentration is monotonically increased. This reveals that the energetic interactions between PNIPA, PEG, and water dominate over the osmotic pressure of mobile counterions. For example, the uncharged gel first deswells slightly with increasing ϕ from 0 to 0.3. If ϕ crosses 0.3, the gel undergoes a collapse transition and remains in the collapsed state up to $\phi = 0.6$. If ϕ is further increased, the gel starts to swell again until ϕ becomes equal to unity. Figure 1 also shows that the range of ϕ, in which the reentrant phase transition occurs, becomes smaller, if charged units are incorporated into the network chains.

Similar swelling curves were also observed at various temperatures. For example, in Figure 2, the swelling ratio of the gels V/V_o and the partition parameter ν_3/ϕ, both measured at 50^0C, are plotted as a function of ϕ. The swelling measurements were conducted using PNIPA gels with 0 and 6 mol% AMPS. Note that the partition parameter ν_3/ϕ represents the ratio of the volume fraction of PEG in the gel phase (ν_3) to that in the solution phase ϕ; thus, $\nu_3/\phi = 1$ means that the PEG concentration inside the gel is equal to that in the solution whereas $\nu_3/\phi = 0$ means that the gel excludes all the PEG molecules.

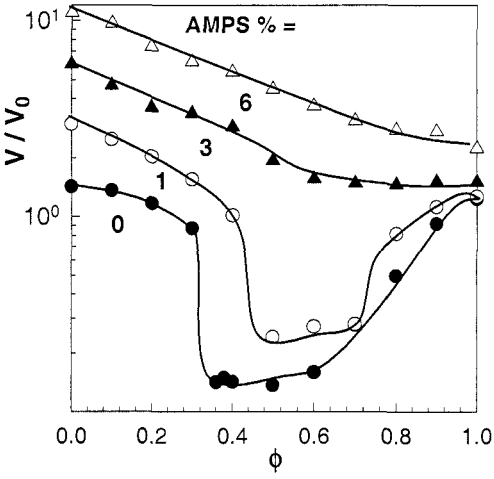


Figure 1. The swelling ratio V/V_0 of PNIPA gels shown as a function of PEG-300 concentration in the external solution. The AMPS contents of the hydrogels are indicated in the Figure. Swelling temperature = 25°C

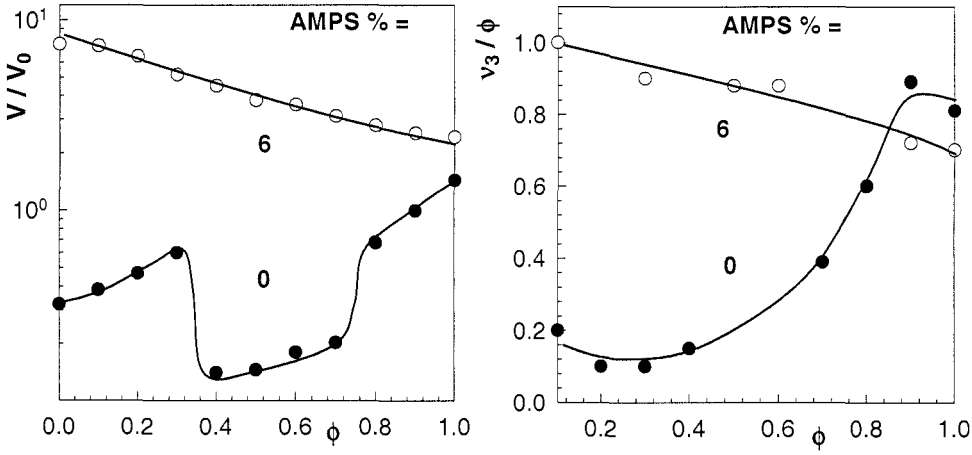


Figure 2. The swelling ratio V/V_0 of PNIPA gels and the partition parameter ν_3/ϕ shown as a function of PEG-300 concentration in the external solution. The AMPS contents of the hydrogels are indicated in the Figure. Swelling temperature = 50°C.

Since the swelling temperature (50°C) is above the lower critical solution temperature (LCST) of PNIPA, the non-ionic PNIPA gel is in collapsed state in water. Addition of PEG-300 into water slightly increases the gel volume up to $\phi = 0.3$. If ϕ is further increased, a collapse transition was observed, followed by a swelling transition at $\phi > 0.7$. On the other hand, the partition parameter ν_3/ϕ for the non-ionic gel is much smaller than unity for ϕ values below 0.7, indicating that the linear chains mainly remain in the solution phase. This is due to the fact that the conformational entropy of a single chain in the solution is much higher than that in the collapsed gel. However, as ϕ is further increased, i.e., as the gel starts to swell again in PEG solution, the partition parameter increases. Thus, the linear chains penetrate into the hydrogel due to the increasing number of arrangements available to the PEG chains penetrating into the swollen gel. In contrast to the uncharged gel, the ionic gel is swollen in water at

50^0C and remains in the swollen state over all range of ϕ. Due to the large volume of the ionic PNIPA gel, PEG chains can easily penetrate into the network without an essential loss of their conformational entropy so that the partition parameter is close to unity (Figure 2).

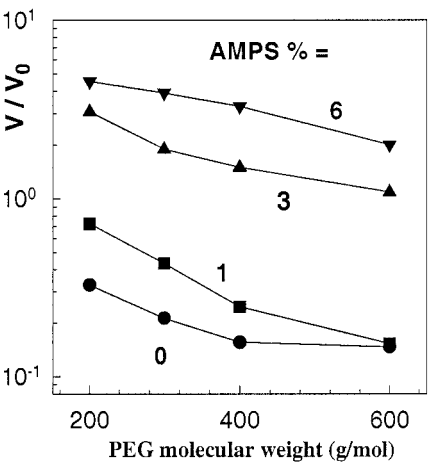


Figure 3. The swelling ratio V/V_0 of gels shown as a function of the molecular weight of PEG in the aqueous PEG solution of $\phi = 0.7$. The AMPS contents are indicated in the Figure. Temperature = 30^0C.

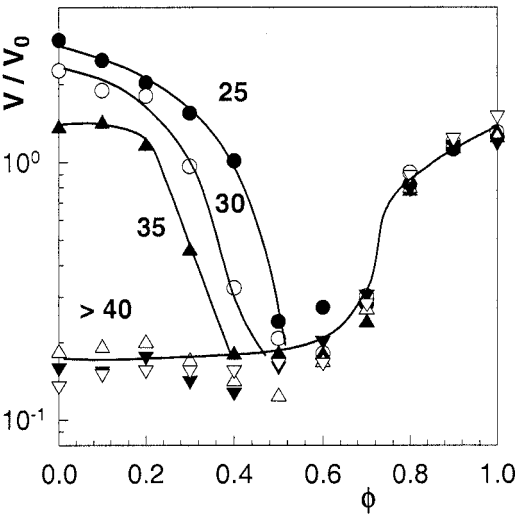


Figure 4. The swelling ratio V/V_0 of gels with 1 % AMPS shown as a function of the PEG-300 concentration ϕ in the external solution. The swelling temperatures (^{0}C) are indicated.

Effect of the molecular weight of PEG

The swelling measurements were also carried out in aqueous solutions of PEG of various molecular weights between 200 and 600 g/mol. In Figure 3, the swelling ratio of PNIPA gels is plotted against the molecular weight of PEG in the external solution of $\phi = 0.7$. The hydrogel slightly deswells as the molecular weight of PEG increases. This was expected due to the effect of the mixing entropy of the linear polymers. As was shown recently, if the molecular weight of linear polymer is sufficiently high, the linear polymer does not penetrate inside the gel, which results in the collapse of the gel in polymer solution [5,6]. However, in the range of the molecular weights studied here, the effect of molecular weight on the gel swelling seems to be insignificant.

Effect of the temperature

In Figure 4, the swelling ratio of gels with 1 mol% AMPS is plotted against the PEG-300 concentration in the solution. Experimental data were for various temperatures between 25 and 60^0C. In Figure 5, both the swelling ratio and the partition parameter are plotted against the PEG-200 concentration in the external solution for two different temperatures, namely one below and the other above the LCST of the ionic PNIPA gel.

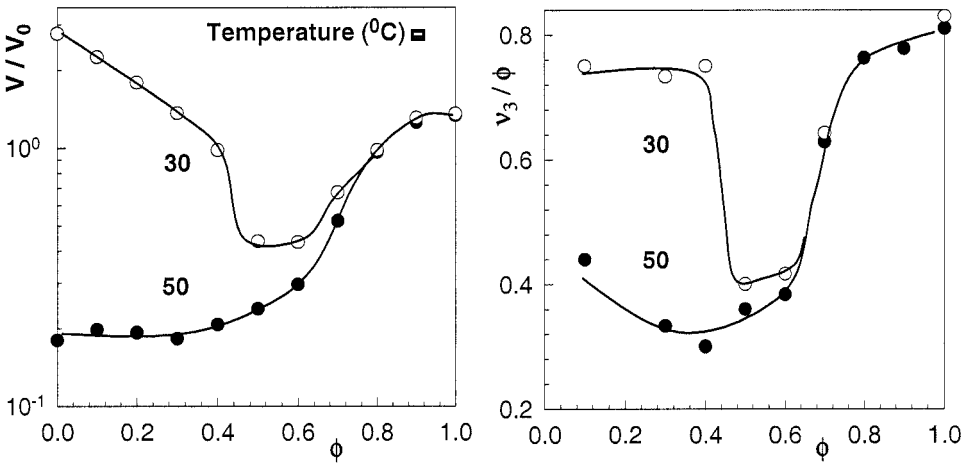


Figure 5. The swelling ratio V/V_o of gels with 1 % AMPS and the partition parameter ν_3/ϕ shown as a function of the PEG-200 concentration in the external solution. The swelling temperatures are indicated in the Figure.

If the swelling temperature is below the LCST of PNIPA, the gel is in swollen state both in water and PEG and exhibits reentrant swelling transition in mixtures of PEG and water. Moreover, the collapse and re-collapse transitions in PNIPA gel are accompanied with a jumpwise change in the partition parameter values ν_3/ϕ (Figure 5). A rapid decrease in ν_3/ϕ, i.e., in the content of the PEG in the gel phase, observed at ϕ = 0.4 – 0.5, results in the collapse of the gel. Conversely, the PEG content of the gel rapidly increases during the re-collapse process. Thus, PEG first flows from the gel to the solution but then reenter the gel as ϕ is continuously increased. At temperatures above the LCST of PNIPA, the gel is in a collapsed state up to a critical PEG concentration above which the gel undergoes a swelling transition. Moreover, the partition parameter ν_3/ϕ is very small for the collapsed PNIPA, i.e., linear polymer is not absorbed by the gel below the critical PEG concentrations, above which - simultaneously with the swelling transition - the partition parameter rapidly increases and approaches to unity. Another interesting feature is that the gels become temperature-insensitive if the PEG concentration in the external solution is above 0.6 (Figure 4).

Comparison of the theory of swelling equilibrium and experiment

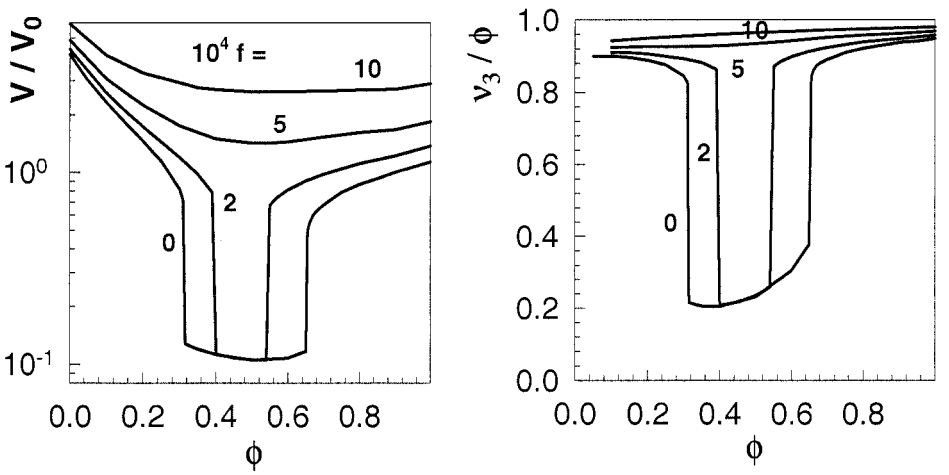
For comparison of the experimental data with theoretical prediction, we use the theory discussed in Refs [5,6,8,9]. This theory predicts the free energy of swelling ΔG as a sum of three terms:

$$\Delta G = \Delta G_m + \Delta G_{el} + \Delta G_i \qquad (1)$$

ΔG_m is the change in the free energy of mixing of water, PNIPA network, and PEG (components 1, 2, and 3, respectively). The energetic interactions between these components are represented by the interaction parameters χ_{12}, χ_{13}, and χ_{23}. ΔG_{el} is the

free energy change due to the elastic deformation of the network chains composed of N segments. ΔG_i is the free energy change due to the nonequal distribution of mobile counterions between the inside and outside of the gel. In the free energy change ΔG, we have neglected the contributions of both non-Gaussian effects of polymer configuration and electrostatic interaction between charges [10], although more elaborative models should contain those contributions. For the following calculations, the PEG concentration in the external solution ϕ, the swelling temperature T, and the charge density of the hydrogels f are taken as the independent parameters. The number of segments in the linear polymer was set to 15, which corresponds to PEG-300. The following system specific parameters reported before were used: $\nu_2^0 = 0.059$ [11], $N = 1330$ [11], $\chi_{23} = 0.026$ [12], $\chi_{12} = 3.415 - 902.2/T + 0.518\nu_2$ [1], where T is the swelling temperature and ν_2 is the volume fraction of crosslinked polymer in the swollen gel, i.e., $\nu_2 = \nu_2^0 / (V/V_o)$. The only adjustable parameter for the present system was the interaction parameter between water and PEG-300 (χ_{13}). χ_{13} was evaluated by fitting the theory to the experimental swelling data of the non-ionic PNIPA gel in PEG – 300 solutions at 25°C. In such way, the value of $\chi_{13} = 0.123$ was found.

Figure 6. The swelling ratio V/V_o and the partition parameter ν_3/ϕ shown as a function of the



PEG-300 concentration in the external solution. The charge densities of the hydrogels f are indicated in the Figure. Temperature = 25°C.

The calculation results are given in Figure 6 as the dependencies of both V/V_o and ν_3/ϕ on the PEG concentration in the solution ϕ. Calculations were for various network charge densities f. Comparison of Figure 6 with the experimental curves given in Figures 1 and 2 shows that the theory qualitatively predicts what we observed experimentally. In agreement with the experiments, reentrant phase transition in the hydrogels appears at low ionic group contents while the gels remain in swollen state at higher ionic group contents. Figure 7 shows V/V_o and ν_3/ϕ versus ϕ plots calculated for two different temperatures, one below and the other above the LCST of PNIPA. Comparison of Figure 7 and Figure 5 shows that the theory is in good agreement with

the experimental data. According to Figure 7, if the temperature exceeds the LCST of PNIPA, the linear polymer chains cannot enter into the collapse PNIPA gel. As a result, linear polymer accumulates in the solution and compresses the PNIPA gel. The swelling transition of the gel observed above a critical polymer concentration indicates that the favorable PEG – PNIPA interactions, represented by $\chi_{23} = 0.026$, compensate more than the large losses in entropy of PEG molecules entering the gel. Thus, in concentrated solutions, PEG penetrates into the gel and results in gel swelling. Calculation results indicate that the PNIPA gels exhibit reentrant swelling transition in PEG solution due to the attractive PNIPA – PEG and water - PEG interactions, represented by the small values of χ_{23} and χ_{13} parameters.

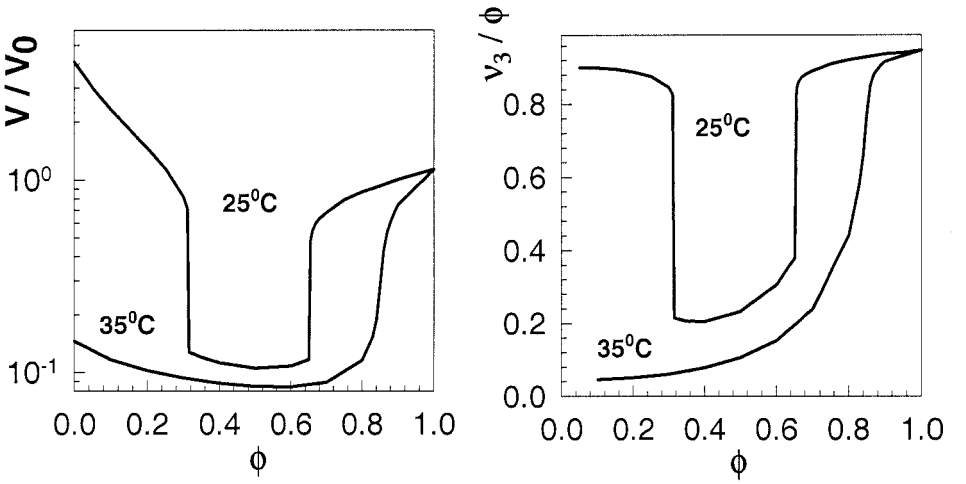


Figure 7. The swelling ratio V/V_o of the non-ionic gel and the partition parameter ν_3/ϕ shown as a function of the PEG-300 concentration in the external solution. The swelling temperatures are indicated in the Figure.

Acknowledgements. The work was supported by Istanbul Technical University Research Fund, contract grant number 1054.

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