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Phase Transition of Hydrolyzed Polyacrylamide Gels in Aqueous Solutions of Poly(ethylene glycol)

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Hydrolyzed polyacrylamide gels immersed in aqueous solutions of poly(ethylene glycol) (PEG) of molecular weight 300 exhibit a discontinuous volume change upon continuous increase of the PEG concentration in the external solution. As the duration of hydrolysis increases, that is, as the proportion of the ionic groups on the network chains increases, the critical concentration of PEG required for a discontinuous volume change rises and, also, the magnitude of the volume collapse becomes larger. Experimental results indicate that the gel collapse in PEG solution is due to the osmotic deswelling of the ionic gel rather than due to a complex formation between polyacrylamide and PEG chains.

Introduction

Hydrophilic gels called hydrogels have widespread applications in medical, pharmaceutical and related fields. In recent years, particular interest has been devoted to the swelling and collapse phenomena that are observed when a hydrogel network is brought into contact with a solvent. The possibility of a first-order volume phase transition in hydrogels has been predicted theoretically[1-5] and proved experimentally on hydrolyzed polyacrylamide (PAAm) gels immersed in acetone - water mixtures[6-10]. In such a first-order phase transition, a change in an external variable like pH, solvent composition, ionic strength or temperature can induce a discontinuous change in the volume of the swollen gel[11,12].

Recently, we have shown that poly(acrylamide-co-acrylic acid) (PAAm-co-PAAc) gels immersed in aqueous solutions of poly(ethylene glycol) (PEG) may also undergo a discontinuous volume change[13]. The distribution of PEG inside and outside the gel phase also changed discontinuously at the phase transition region. The experimental results were found to be in qualitative agreement with the calculations based on the Flory - Huggins theory[14]. Therefore, we concluded that the collapse of PAAm-co-PAAc gels in PEG solution is due to the osmotic deswelling of the ionic gel[13]. However, it was suggested that a complex formation between PEG and PAAc chains may also be the reason for the polymer collapse[15]. According to this point of view, the complexation between long sequences of carboxylic acid groups and ether oxygen atoms results in the volume phase transition of the gel in PEG solutions.

The present work aims to answer the question about which mechanism is operative for the collapse transition of PAAm-co-PAAc gels in aqueous PEG solution. Since complexation is produced only by

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carboxylic acid groups in the undissociated state[16,17], we prepared hydrolyzed PAAm gels. It is known that hydrolysis of PAAm gels in a basic solution converts some of the pendant amide groups into the carboxylate anions[18–20]. The fractional conversion of the amide groups depends on the time of hydrolysis. It was shown that both the time of hydrolysis, τ, and the pH of the NaOH solution have a decisive influence on the collapse behavior of PAAm gels in acetone-water mixtures. For instance, hydrolysis at a higher pH was reflected in the formation and extent of the collapse much more distinctly ($\tau \sim$ 10 days at pH = 12 correspond to ($\tau \sim$ 60 days at pH = 8-9)[19]. The maximum conversion of the amide groups is reported to be 25 %; at pH = 12 this value is observed after 60 days[18]. In the present study, hydrolysis of PAAm gels was carried out in aqueous solutions of NaOH with pH = 10.7 and 12 for various times. The swelling behavior of hydrolyzed PAAm gels in PEG solution was investigated as a function of the hydrolysis time of the gels and the PEG concentration in the medium. If complexation were the reason of the polymer collapse, dissociated acid groups on the network chains would prevent the collapse of the gel in PEG solution. As will be shown below, hydrolyzed PAAm gels also exhibit discrete volume change in response to an infinitesimal change in PEG concentration in the outer solution.

Experimental

Materials

Acrylamide (Merck) was purified by recrystallization from acetone/ethanol mixture (7/3 volume ratio). All other materials, N,N'-methylenebis(acrylamide) (BAAm, Fluka), ammonium persulfate (APS, Aldrich), N,N,N',N'-tetramethylethylenediamine (TEMED, Aldrich) and PEG of molecular weight 300 g/mol (Fluka, PEG 300) were used as received. The polymerization solvent water was distilled twice before use.

Methods

Non-ionic PAAm gels were prepared by free-radical crosslinking copolymerization of acrylamide with a small amount of BAAm in aqueous solution. APS and TEMED were used as the initiator and the accelerator, respectively. The reactions were carried out at room temperature ($21 \pm 2\,^{\circ}$C). The gels were prepared according to the following procedure:

5 g acrylamide, 133 mg BAAm, and 40 mg APS 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. Gelation took place within 5 min. After 3 hours, the gels were cut into specimens of approximately 10 mm in length and immersed in a distilled water for 1 h to remove the unreacted species. It was found that the sol fraction in the gels is less than 0.1 % after extraction with water.

To convert the non-ionic PAAm gels into ionic (hydrolyzed) gels, gel samples of 5.8 mm in diameter and approximately 10 mm in length were placed in aqueous solutions of NaOH with a pH of 10.7 and 12. After predetermined hydrolysis times, the gels were washed with distilled water for several times until neutral pH in the external solution was obtained.

Swelling measurements

Hydrolyzed PAAm gel samples swollen in water were placed in vials (100 mL) filled with a PEG - water solution. The aqueous solutions of PEG exhibited a pH value of 6.5 - 7.0. The volume of solution in the

vial was much larger than the gel volume so that both the concentration and the pH of the solution were practically unchanged. The vials were set in a temperature-controlled bath at $25.0 \mp 0.1\,^{\circ}$C. In order to reach the equilibrium degree of swelling, the gels were immersed in solutions for at least one week. The diameter of the gels was measured by a calibrated digital compass and the equilibrium swelling ratio of the gels, V/V_0, where V and V_0 are the volumes of gel at equilibrium and after preparation, respectively, was calculated as

$$V/V_0 = (D/D_0)^3, \tag{1}$$

where D and D_0 are the diameter of the gels after equilibrium swelling and after preparation of the original non-ionic gel (5.8 mm), respectively. Each swelling ratio reported in this paper is an average of at least two separate measurements; standard deviations of the measured swelling ratios were less than 10 and 5% of the mean for swollen and collapsed gels, respectively.

Results and Discussion

In the present study, non-ionic PAAm gels were placed in aqueous solutions of NaOH with pH = 10.7 and 12 for various times to produce ionic groups on the network chains. This procedure leaves the crosslink density of the PAAm network unchanged. In Figure 1, variation of the equilibrium swelling ratio of the gels in distilled water, V/V_0 is shown as a function of the time of hydrolysis in aqueous NaOH solution with pH = 10.7. V/V_0 increases rapidly with rising hydrolysis time up to about 8 days. This is due to the increasing number of ionic groups on the network chains with increasing hydrolysis time. Thus, since the mobile ion (Na^+) concentration within the ionic network is higher than in the surrounding solution (water), the osmotic pressure that this creates causes more water to enter the network and expand it. As the hydrolysis time further increases, V/V_0 slightly increases and, after about 20 days, the swelling ratio becomes rather insensitive to the time of hydrolysis.

The gels isolated at different degrees of hydrolysis were then used for equilibrium swelling experiments in aqueous solutions of PEG of molecular weight 300. Variation of the equilibrium swelling ratio of the gels, V/V_0, with the PEG 300 concentration in the external solution is shown in Figures 2 and 3 for various hydrolysis times. The hydrolysis was carried out at pH 10.7 (Figure 2) and 12 (Figure 3). The volume of the gel phase decreases upon increase of the PEG concentration. Starting after one day or two days of hydrolysis at pH = 12 and 10.7, respectively, this decrease becomes discontinuous. The critical value of the PEG concentration at which discrete transition takes place increases and the magnitude of collapse becomes larger as the time of hydrolysis increases. For prolonged hydrolysis times the gels remain in the swollen state (Figure 3) or deswell only slightly (Figure 2) over the entire range of the external PEG concentration.

As pointed out in the Introduction, there are two possible reasons for the contraction of PAAm gels 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. Polycarboxylic acids such as poly(methacrylic acid) (PMAAc) or poly(acrylic acid) (PAAc) have long been known to form complexes with PEG under appropriate conditions of pH[17,21–26]. The formation of intermolecular complexes between PMAAc gel and PEG is also a well known phenomenon and results in the collapse of the gel[17]. However, the stability of such complexes lowers sharply with the decrease of the degree of polymerization of PEG chains or with the increase of the pH of the solution. For instance, PEG with molecular weight of 7500 or lower does not form a complex with PAAc[27,28]. Moreover, complexation is produced only by carboxylic groups in the undissociated state[16] In the present study, since the carboxylic

acid groups on the network chains are in dissociated state, we can conclude that the contraction of the gel in PEG solution is due to the osmotic deswelling of the gel (no complex formation). Since the hydrolysis time is proportional to the number of ionic groups produced on the network chains[18], the results are in agreement to those obtained earlier with poly(acrylamide-co-acrylic acid) gels[13].

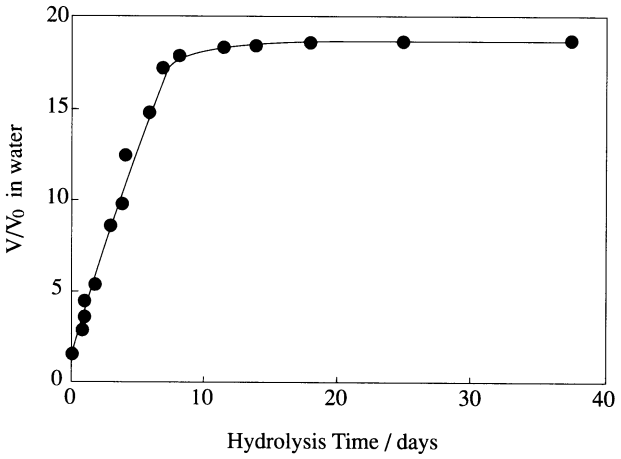

Figure 1. Variation of the equilibrium swelling ratio, V/V_0, of the gels in water with the time of hydrolysis of non-ionic PAAm gels in aqueous NaOH solution (pH =10.7).

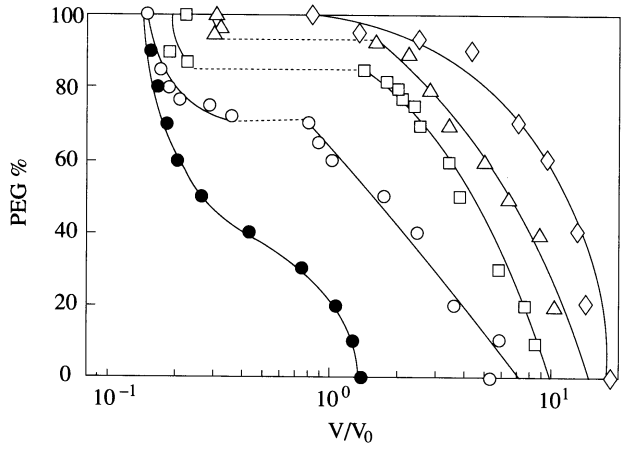

Figure 2. Variation of the swelling ratio, V/V_0, of hydrolyzed PAAm gels with the concentration of PEG 300 in the outer solution. PEG concentrations are in v/v %. pH of NaOH solution used in the hydrolysis is 10.7. Hydrolysis times = 0 (•); 2 (○); 7 (□); 18 (△and 38 days (◇).

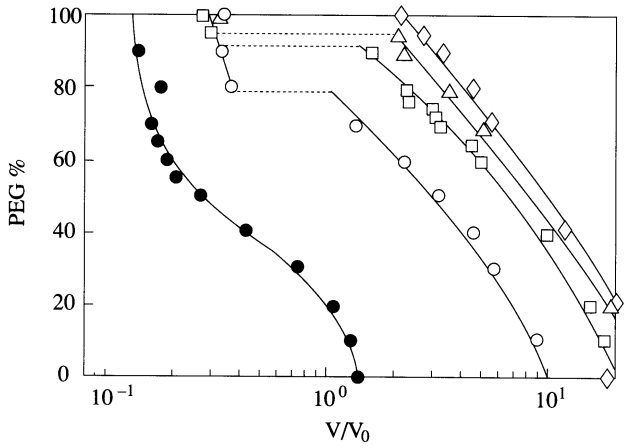

Figure 3. Variation of the swelling ratio, V/V_0, of hydrolyzed PAAm gels with the concentration of PEG 300 in the outer solution. PEG concentrations are in v/v %. pH of NaOH solution used in the hydrolysis is 12. Hydrolysis times = 0 (•); 1 ○; 5 (□); 9 (△); and 16 days (◇).

To interpret the experimental data, we use the classical Flory-Huggins (FH) 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[14]

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

where n_i is the moles of the species i, ν_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 (water), the network (PAAm), and the linear polymer (PEG), respectively. For the free energy of deformation ΔG_{el}, several theories are available. However, we will use here the simplest affine network model to describe qualitatively the behavior of PAAm gels[14]:

$$\Delta G_{el} = (3/2)(RT/NV_1)\left((\nu_2^0/\nu_2)^{2/3} - 1 - \ln(\nu_2^0/\nu_2)^{1/3}\right), \tag{4}$$

where N is the average number of segments in the network chains, V_1 is the molar volume of solvent, ν_2 and ν_2^0 are the volume fraction of polymer network in the equilibrium swollen gel and after preparation, respectively. For weakly charged ionic gels, the free energy of electrostatic interactions, ΔG_i, may be written as follows[14]:

$$\Delta G_i = RT\frac{f}{N}\frac{\nu_2}{\nu_1} n_1 \ln(f\nu_2/N), \tag{5}$$

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

Substitution of eqs. 3 - 5 into eq. 2 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:

$$\frac{\Delta\mu_1^{gel}}{RT} = N^{-1}(\nu_2^{1/3}\nu_2^{0^{2/3}} - \nu_2/2) + \ln\nu_1 + (1-\nu_1) - \nu_3/y + (\chi_{12}\nu_2 + \chi_{13}\nu_3)(1-\nu_1) - \chi_{23}\nu_2\nu_3 - \nu_2 f/N \tag{6a}$$

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

$$\frac{\Delta\mu_1^{gel}}{yRT} = N^{-1}(\nu_2^{1/3}\nu_2^{0^{2/3}} - \nu_2/2) + (1/y)\ln\nu_3 + (1/y)(1-\nu_3) - \nu_1 + (\chi_{13}\nu_1 + \chi_{23}\nu_2)(1-\nu_3) - \chi_{12}\nu_1\nu_2 - \nu_2 f/N \tag{7a}$$

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

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:

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

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

The system of equations represented by eq 8 has been solved numerically to calculate the swelling ratio of PAAm gels in aqueous PEG solutions ($V_{V_0} = \nu_2^0/\nu_2$). For calculations, the values used were $\nu_2^0 = 0.035$ (estimated assuming additivity of the volumes of water and PAAm, $\rho = 1.42$ g/mL), $\chi_{12} = 0.48$[29], and $\chi_{13} = 0.45$[30]. 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 eq 6a for the condition $\nu_3 = 0$ and $\Delta\mu_1^{gel} = 0$. The value $\nu_2 = 0.049$ found by experiments yielded $N = 165$. N was held constant at this value in the calculations described here since the degree of hydrolysis does not alter the network topology. It was also assumed that y is equal to the degree of polymerization of the PEG 300 chains ($y = 6.4$). 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[13], was used throughout this study. For ionic gels and for certain values of ϕ, eq 8 is satisfied by three values of both ν_2 and ν_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.

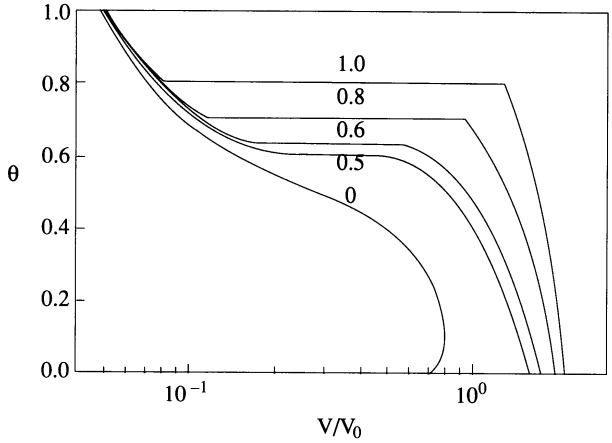

Figure 4. Volume fraction of PEG 300 in the external solution (ϕ) versus swelling ratio V/V_0 plot for a series of values of f, which is proportional to the time of hydrolysis of non-ionic PAAm gels. Calculations from eqs 8a and 8b for $y = 6.4$.

Results of calculations for ionic PAAm gel - PEG 300 - water system are presented in Figure 4. Here, volume fraction of PEG 300 in the external solution (ϕ) versus V/V_0 plot is shown for a series of f values, which is proportional to the amount of ionizable group incorporated into the network, i.e., to the hydrolysis time of non-ionic PAAm gels. 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 counterions. Therefore, PEG chains can penetrate the swollen ionic gels without essential loss in conformational entropy. A discrete first-order phase transition is observed only if f exceeds a critical value. As f increases, i.e., as the time of hydrolysis increases, the jump in V/V_0 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 present study. 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.

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