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Heterogeneities in polyacrylamide gels immersed in acetone-water mixtures

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Summary

Immersion of polyacrylamide gels in acetone-water mixtures with a high content of acetone leads to the formation of heterogeneous structures. The extent of heterogeneity increases as the initial swelling degree of the gel increases, or, as the polarity of the nonsolvent decreases. The nature of the deswelling curves indicates that the polymer-rich regions of the gel formed by the collapse transition block the solvent diffusion outside the gel. This prevents the equilibration of the gel volume with surroundings.

Introduction

Hydrophilic gels called hydrogels have received considerable attention for use as specific sorbents and as support carriers in biomedical engineering. In recent years, attention has turned to the swelling and collapse phenomena that are observed when a hydrogel network is brought into contact with a solvent. The possibility of a first-order phase transitions in polymer gels has been predicted theoretically (1) and proved experimentally on hydrolyzed polyacrylamide (PAAm) gels immersed in acetone - water mixtures (2).

Theoretical analysis of the experimental swelling data of polymer gels assumes that the gel immersed in a liquid attains its thermodynamic equilibrium state with the surrounding solution after a finite time, i.e., usually after a few weeks. Thereafter, since the chemical potentials of all diffusable components in and outside the gel sample are equal, theories predict the equilibrium volume of the gel phase as a function of the solvent composition. However, due to the prolonged relaxation time of the network chains compared to that of linear chains, nonequilibrium states may appear in polymer gels. These nonequilibrium states may be fixed if additional crosslinks are introduced into the gel (3) or, if these states become kinetically frozen (4). Ilavky (5) showed that, if PAAm gels are immersed in mixtures with a high content of acetone, the gel samples remain heterogeneous even after 2 months of observation. No further details or experimental data were given by this author. Philippova et al. (6) also observed the appearance of heterogeneities in swollen ionic gels immersed in poor solvents. They showed that water swollen gels immersed in water-ethanol mixtures with ethanol contents higher than 70 % exhibit kinetically frozen nonequilibrium structures. Formation of non-equilibrium structures was also observed by Siegel et al. in pH-sensitive gels (7). Recently, we have shown formation of heterogeneous structures in PAAm gels immersed in aqueous solutions of poly(ethylene glycol) (8).

The present work aims to describe the conditions for the formation of nonequilibrium structures in PAAm gels. For this purpose, a series of PAAm gels with different ionic group contents were prepared by solution polymerization technique. The gels were then subjected to swelling/deswelling experiments, starting from three different initial states: a) the dry state, b) the state after preparation, and c) the equilibrium swollen state in pure water. The solvents used for the experiments were acetone-water mixtures of various compositions, methanol, ethanol, and n-butanol. Assuming that a gel sample attains its equilibrium state in a given solvent, the final mass of the gel should be independent on its initial state. Deviations from this condition will give information about the extent of heterogeneities in PAAm gels. Here, we report the effects of the number of ionic groups and of crosslinks in the gel as well as the polarity of the nonsolvent on the degree of the heterogeneities in PAAm gels.

Experimental

PAAm gels

PAAm gels were prepared by free-radical crosslinking copolymerization of acrylamide with a small amount of N,N'-methylenebis(acrylamide) (BAAm) in aqueous solution. Sodium acrylate (NaAc) was used as the ionizable comonomer and prepared *in situ* by adding equimolar amounts of sodium hydroxide (NaOH) and acrylic acid (Ac) in the polymerization mixture. Ammonium persulfate (APS) and N,N,N',N'-tetramethyl-ethylenediamine (TEMED) were respectively the initiator and the accelerator. The reactions were carried out at room temperature (21±2°C). The gels were prepared according to the following scheme: 5 g acrylamide, 133 mg BAAm, 40 mg APS and varying amounts of NaOH and Ac were dissolved in double distilled water to give a total volume of 100 mL. After addition of 0.24 mL of TEMED, the solution was transferred to small tubes of 5.8 mm in diameter. The gelation took place within 5 min. After 3 hours, the gels were cut into specimens of approximately 10 mm in length and divided into two parts. The first part of the gel samples, which we shall call thereafter “gels after synthesis”, was subjected to swelling experiments without further treatment. The second part of the gel samples was immersed in a large excess of distilled water to remove the unreacted species. It was found that the sol fraction in the gels is less than 0.1 % after extraction with water. Then, a part of the equilibrium swollen gels in water, called “preswollen gels”, were used for swelling experiments. Another part of the preswollen gels was successively washed with acetone-water mixtures containing increasing amounts of acetone and, finally with pure acetone. Using this solvent exchange procedure, the good solvent water in the preswollen gels was gradually replaced by the nonsolvent acetone; thus, the gel was transferred from rubbery to the glassy state without the appearance of heterogeneities. The gels were then dried in vacuum at room temperature. Thereafter the gel specimens, called “dry gels” were used for the swelling experiments. Swelling experiments were also carried out using gel samples dried in vacuum at room temperature after their preparation. The swelling behavior of these samples was found to be the same as that of the dry gels.

Swelling measurements

For the swelling measurements, PAAm gel samples of different initial states (preswollen gels, dry gels, and gels after synthesis) were immersed in vials (100 mL) filled with acetone-water mixtures. The volume of solution in the vial was much larger than the gel volume so that the concentration of the acetone-water mixture was practically unchanged. For the swelling experiments in nonsolvents (acetone, methanol, ethanol and n-butanol), the nonsolvent was refreshed every other day over a period of one week to keep the concentration constant. The swelling experiments were carried out at 21±2°C.

In order to reach the apparent equilibrium degree of swelling, the gels were immersed in solutions at least for one week. The relative mass of the gel after swelling is expressed in terms of the swelling ratio related to the network formation state, q_w, which is defined as $q_w = m / m_0$, where in and m_0 are the masses of the gel after swelling and after preparation, 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 Figure 1, the relative masses of PAAm gels, q_w, of different initial states are shown as a function of the acetone concentration in the outer acetone-water mixtures. The concentrations of the ionic comonomer NaAc in the monomer mixture were 0, 4.6, and 28 mol % in A, B, and C, respectively. The filled and empty circles belong to dry and preswollen gels respectively, whereas the filled triangles to the gels after synthesis. As expected (9, 10), the PAAm gel without any ionizable groups exhibits a continuous change in the relative mass over the entire range of acetone concentration, whereas ionic PAAm gels undergo a discontinuous phase transition at a critical acetone concentration. For acetone concentrations at or below the critical acetone content for phase transition, all gel samples exhibit similar behavior within the limits of experimental error; all are in a swollen state below the critical acetone concentration, whereas a sudden change in the relative mass of the gel was observed at the critical acetone content. These results indicate that all the gel samples are at equilibrium in this range of acetone concentrations. The discrepancy in the relative masses of the gels appears after passing the phase transition point. The "dry" gels slightly decrease their relative masses as the acetone content of the solvent mixture further increases, whereas the preswollen gels cannot deswell up to the equilibrium state. The swelling degree of PAAm gels immersed in acetone-water mixtures after their preparation lies between the two sets of experiments. Comparison of the ionic gel masses in acetone indicates that the amount of solvent in the preswollen gels is about tenfold larger than in the gels after synthesis or after drying.

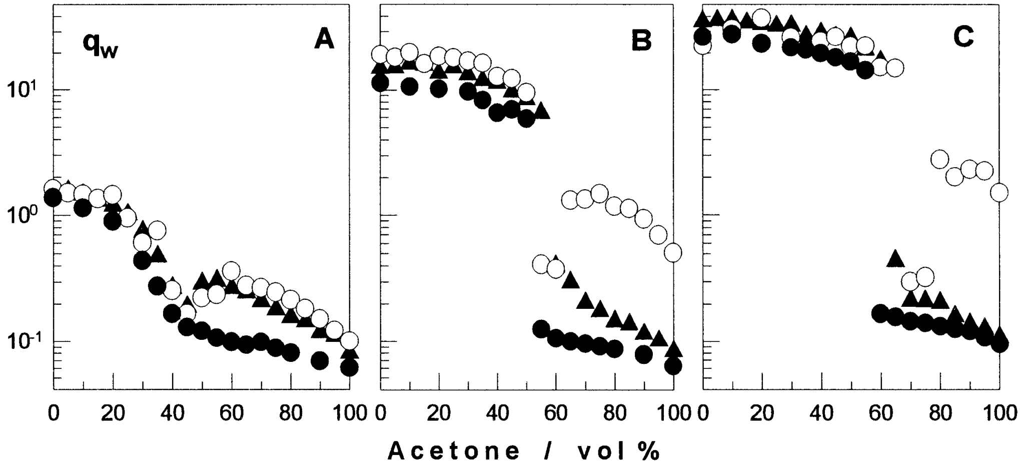
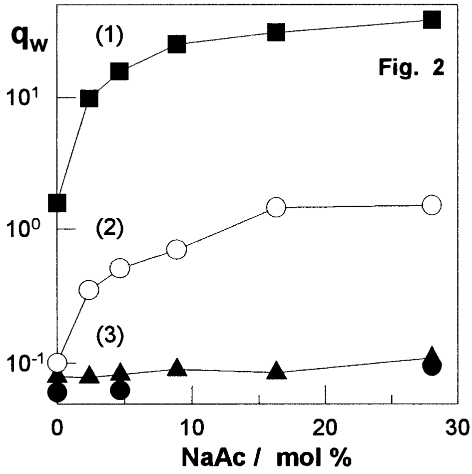


Fig. 1. The relative masses, q_w, of PAAm gels of different initial states shown as a function of the acetone concentration in the acetone-water mixtures. BAAm = 1 mol %, NaAc = 0 (A), 4.6 (B), and 28 mol % (C). Initial states of the gel = dry (●), preswollen (○), after synthesis (▲).

Even after 7 months of immersion times in acetone, no change in the relative mass of the preswollen gels was observed, indicating that they are at an "apparent equilibrium state" in acetone. Thus, the originally swollen gel fails to deswell to the same mass as is observed when deswelling is from the dry or after synthesis states. Assuming that the volume of the gel in acetone does not change on removing the extra solvent, for instance, by freeze-drying, this process would lead to a porous hydrogel in which the porous structure was created during the posttreatment of the gel samples.

According to the above results, heterogeneity in PAAm gels starts to appear after the phase transition point is crossed. Visual observations showed that heterogeneous gel samples exhibit both swollen (rubbery) and unswollen (glassy) regions; thus, both swollen and collapsed states coexist in a single sample beyond the critical point. A series of gels containing varying amounts of the ionic comonomer NaAc between 0 and 28 mol % were prepared and then subjected to swelling experiments starting from different initial states. All gel samples exhibited similar behavior in acetone-water mixtures, as illustrated in Figure 1. In Figure 2, the relative masses of the gels, q_w, in water as well as in acetone are shown as a function of their NaAc contents. As expected, q_w of PAAm gels in water increases as the ionic group content increases because of the additional swelling due to the osmotic pressure of counterions. At NaAc contents as high as 17%, q_w in water becomes rather insensitive to the ionic group content of the gel as a result of the counterion condensation (11) or due to the finite extensibility of the network chain. In acetone, the relative mass of dry gels or gels after synthesis remains constant over the entire range of NaAc concentration; this is due to the low polarity of acetone compared to water which facilitates formation of ion pairs on the network chains and prevents the extra swelling of ionic gels. However, the relative mass of preswollen gels in acetone increases with increasing NaAc content of the gel up to about 17 mol % and then remains constant.



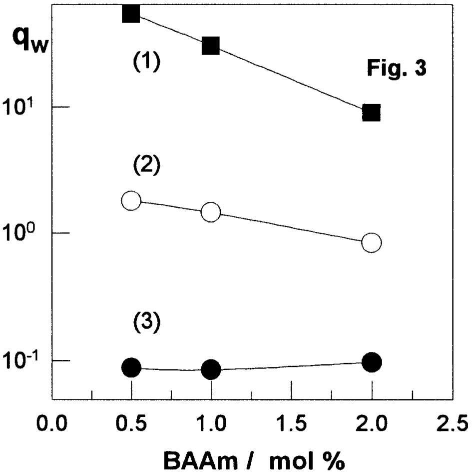


Fig. 2. The relative masses of PAAm gels, q_w, shown as a function of their NaAc contents. The curve (1) concerns the gels in water while the other two curves (2, 3) demonstrate the behavior of the gels in acetone. Initial states of the gel: dry (●), preswollen (○), after synthesis (▲). BAAm = 1 mol %.

Fig. 3. The relative masses of PAAm gels, q_w, shown as a function of their BAAm content. NaAc = 16.5 mol %. See legend to Figure 2 for the explanations.

The heterogeneity in the gel may be characterized by the difference between the relative masses of the preswollen and dry gels. According to Figure 2, this difference increases with increasing ionic group content of the gel. This means that increasing swelling ratio in water also increases the extent of heterogeneities in preswollen PAAm gels immersed in acetone. In Figure 2, increase in the water absorption capacity of the gels was achieved by replacing some of the acrylamide units in the network chains with the ionic comonomer NaAc. Similar results were also obtained by decreasing the crosslink density of PAAm gels. In Figure 3, the relative masses of the gel in water and in acetone are shown as a function of the amount of the crosslinker BAAm used in the gel synthesis. Decrease in BAAm content increases the swelling capacity of PAAm gels in water and thus, increases the extent of heterogeneities in PAAm gels immersed in acetone.

In Figure 4, variation of the relative mass of ionic PAAm gel with 28 mol % NaAc content is shown as a function of the contact time with pure acetone. The empty symbols belong to the preswollen gels, whereas the filled symbols are for gel samples used after synthesis. In all ionic gel samples immersed in acetone after their preparation, a two stage deswelling process was observed; a fast initial period which corresponds to release of water from the excess volume of the rubbery polymer, followed by a slow second stage of deswelling. The gels reach their final swelling state within a couple of days. In preswollen gels, however, the second stage of deswelling was not observed. One may expect that, in the initial period of deswelling, the diffusion of solvent controls the deswelling process and about half of the water content of the gel is released within this period. As deswelling commences and the gel loses water, the glass transition temperature of the polymer/solvent mixture approaches to the temperature of the experiment and the polymer requires a finite time to relax to its final contracted state. Thus, the relaxation time of polymer in response to changes in solvent composition inside the gel becomes rate limiting in the second stage of deswelling.

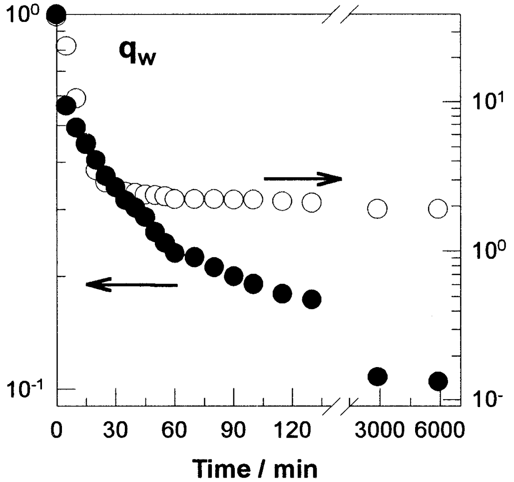


Fig. 4. Variation of q_w of ionic PAAm gel with 28 mol % NaAc shown as a function of the contact time with pure acetone. Initial states of the gel: preswollen (O), after synthesis (●).

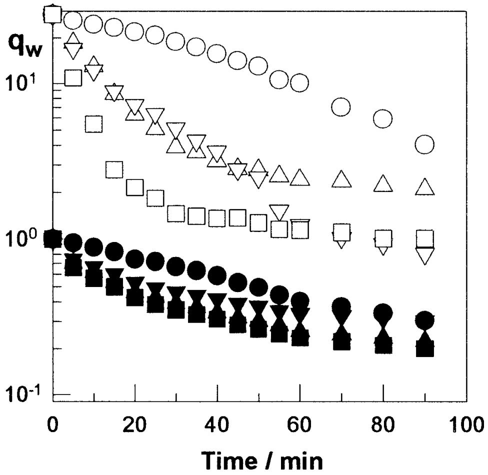


Fig. 5. Variation of q_w of ionic PAAm gel with 16.5 mol % NaAc shown as a function of the contact time with a series of nonsolvents. The empty and filled symbols belong to preswollen gels and gels after synthesis, respectively. Nonsolvents: n-butanol (O), ethanol (Δ), methanol (∇), acetone (□).

According to the experimental results, since the second stage of deswelling was not observed in gels from the swollen state, the glassy regions formed by the collapse transition seems to block the equilibration of the gel volume with surroundings. Thus, the discrepancy in the final relative masses of the gels can be accounted for different relaxation times of the network chains in both gels. Deswelling process from the dry or after synthesis states proceeds by slow relaxation of the whole network chains and further deswelling of the macroscopic sample so that an equilibrium state can be approached. However, in deswelling process from the swollen state, the swollen gel sample on contact with the poor solvent first segregates into a solvent-rich and a polymer-rich phase; if the polymer-rich regions of the sample are in the glassy state, they can block solvent diffusion and so, further deswelling of the whole sample. Thus, microdomains in a glassy state will appear which are embedded in polymer-poor regions in rubbery state so that an equilibrium cannot be reached and the heterogeneous structure is stabilized.

In Figure 5, variation of the relative mass of ionic PAAm gels with 16.5 mol % NaAc content is shown as a function of the contact time with a series of nonsolvents. The empty and filled symbols belong to preswollen gels and gels after synthesis respectively. The form of the deswelling curves strongly depends on the nature of the nonsolvent used. The rate of deswelling increases in the order n-butanol < methanol and ethanol < acetone. In order to understand the type of deswelling curves it is useful to consider the extent of interactions between the nonsolvents and the PAAm segments. According to the Hildebrand theory (12), the solvating (swelling) power of a polymer-solvent medium can be estimated from $(\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are the solubility parameters for the solvent and the polymer, respectively. The solubility of a polymer in a solvent is favored when $(\delta_1 - \delta_2)^2$ is minimized, i.e., when the solubility parameters of the two components are most closely matched. A more detailed solubility parameter approach proposed by Hansen (13) separates the solubility parameter into components due to dispersion (nonpolar) forces (δ_d), polar forces (δ_p), and hydrogen-bonding interactions (δ_h). Materials having similar (Hansen) solubility parameters have high affinity for each other. Thus, the values $\Delta\delta_d^2 = (\delta_{d,1} - \delta_{d,2})^2$, $\Delta\delta_p^2 = (\delta_{p,1} - \delta_{p,2})^2$, and $\Delta\delta_h^2 = (\delta h_{h,1} - \delta_{h,2})^2$ are important in determining the extent of interactions for a solvent (1) - polymer (2) system.

Since water is a good solvent for PAAm, its solubility parameter components can be taken as those of PAAm. Literature data (14) indicate that the dispersion solubility parameter values ($\delta_{d,1}$) of the nonsolvents used are quite similar; thus, nonpolar interactions cannot be responsible for the features of the deswelling kinetics shown in Figure 5. However, polar and H-bonding components of the solubility parameter vary considerable depending on the type of the nonsolvents (14). In Figure 6, the difference between the relative masses of the preswollen gels and the gels after synthesis, Δq_w, after a deswelling time of 1.5h is plotted as functions of $\Delta\delta_p^2$ and $\Delta\delta_h^2$. Since Δq_w is equal to the amount of “frozen solvent” inside the preswollen gels, Figure 6 illustrates the dependence of the degree of heterogeneity in PAAm gels on the extent of polar and H-bonding interactions in gel - nonsolvent system. The heterogeneity appears intensively in butanol, i.e., in nonsolvent with the smallest polarity, and, the degree of heterogeneity decreases as the polarity of the medium increases, i.e. as the value of $\Delta\delta_p^2$ decreases. Previous theoretical studies (15, 16) showed that the degree of ion pairs formation strongly depends on the polarity of the medium; in relatively nonpolar solvents such as in n-butanol, the degree of dissociation of ion pairs in the gel is very small. Thus, decrease in polarity of the nonsolvent increases the probability of ionpairing in the polymer-rich regions of the sample with subsequent shrinkage of these regions. As a result, the polymer-rich regions of the gel will pass into the glassy state earlier, i.e., at higher relative masses, as the polarity of the nonsolvent decreases; this blocks increasingly the release of water from the polymer-poor regions.

The results shown in Figures 5 and 6 also indicate that the gel deswells rapidly in acetone and the degree of heterogeneity in the gel created by this nonsolvent is relatively low. Comparison of the $\Delta\delta_p^2$ values show that acetone is more polar than ethanol and n-butanol (Figure 6); as a result, it induces relatively low degree of heterogeneity in PAAm gels. On the other hand, in contrast to the alcohols used, acetone - PAAm system exhibits a high $\Delta\delta_h^2$ value, i.e., acetone forms weak H-bonds with the acrylamide units of the network chains (Figure 6). This facilitates the movement of individual solvent and nonsolvent molecules through the network and results in the observed rapid deswelling of PAAm gels in acetone (Figure 5).

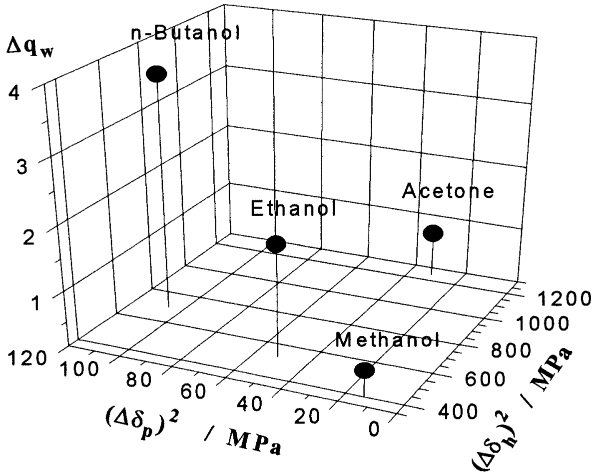


Fig. 6. The difference between the relative masses of the preswollen gels and the gels after synthesis, Δq_w, after a deswelling time of 1.5h shown as functions of $\Delta\delta_p^2$ and $\Delta\delta_h^2$.

Conclusions

Heterogeneous (porous) crosslinked polymers have usually been prepared by crosslinking copolymerization of monomers in the presence of an inert diluent. A phase separation during the copolymerization and crosslinking reactions is responsible for the formation of heterogeneous structures (17,18). The results presented here introduce a novel technique to produce heterogeneous hydrogels in which the heterogeneity was created during the posttreatment of the gel with nonsolvents. The extent of heterogeneity in PAAm gels increases as the initial swelling degree of the gel increases or, as the polarity of the nonsolvent decreases. The nature of the deswelling curves in nonsolvents indicates that the polymer-rich regions of the gel formed by the collapse transition block the solvent diffusion inside the gel. This prevents the equilibration of the preswollen gel volume with surroundings.

It must be noted that the experimental results presented here were obtained using cylindrical PAAm gel samples of 10 mm in length and 5.8 mm in diameter. Since the relaxation time of the network chains is proportional to the macroscopic gel size (10), the data obtained in the non-equilibrium region may not be reproducible for PAAm gel samples of different shape and volumes.

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