

DESWELLING BEHAVIOR OF POLY(TETRAETHYLENEPENTAMINE EPICHLOROHYDRIN) GELS HYDROPHOBICALLY MODIFIED BY STEARIC ACID*

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Abstract A novel type of polysoap hydrogel based on poly(tetraethylenepentamine-epichlorohydrin) hydrophobically modified by stearic acid was prepared. The deswelling behaviors of polysoap hydrogels were studied by immersing the gels in buffer solution at various pHs and ionic species. The deswelling of the gels did not depend on the cationic species of electrolyte but depended strongly on the anionic species. A comparison of polysoap gels with the gel unmodified hydrophobically verified the importance of hydrophobic interaction, which enhances the occurrence of deswelling rate.

Key words pH Sensitive, Polysoap hydrogel, Deswelling, Ionic strength

INTRODUCTION

The swelling and deswelling in aqueous solution are an important property for the intelligent polymer hydrogels. The behavior of swelling/deswelling depends mainly on the effect of the external environment, such as pH, temperature, electric field and so on. In general, polymer hydrogels for pH-sensitive usually contain ionizable acidic and basic pendant groups, such as carboxylic, amino and quaternary ammonium groups, which change their ionization state with the pH, resulting in modification of characteristics of gels.

It is known that there are four kinds of driving forces for the environmentally sensitive in network structure of hydrogels. They are van der Waals interaction, electrostatic interaction, hydrogen bond and hydrophobic interaction^[1]. The competition between inter (intra) molecular repulsion and attraction results in the volume phase transition of hydrogels. When a repulsive force, usually electrostatic in nature, overcomes an attractive force such as hydrogen bond and hydrophobic interactions between network chains, the gel volume increases discontinuously in some cases or continuously in others. Conversely, a decrease in volume may occur when the attractive force becomes dominant.

Many experimental studies of pH dependence of hydrogels have usually employed acrylamide derivative gel that introduces charged groups at low concentration levels in their polymer network. Poly(*N,N*-diethylacrylamide)^[2], poly(*N*-isopropylacrylamide)^[3], partially hydrolyzed polyacrylamide and their copolymers^[4], poly(methacrylic acid)^[5] and poly(*N*-acryloylpyrrolidine)^[6] have been found to show volume phase transition in response to external stimuli. Generally, these gels are hydrophilic types. Little attention has been paid to the polysoap hydrogels.

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Recently, we synthesized some polysoaps and investigated their properties in aqueous solution^[7, 8]. Based on the study of polysoaps, we synthesized a novel type of polysoap hydrogels, poly(tetraethylenepentamine-epichlorohydrin) hydrophobically modified by stearic acid. It contained longer hydrophobic side chains with 18 carbon atoms. Herein, we report the deswelling in buffered solutions as a function of pH, ionic species and strength. The results reveal that the environmental sensitivity of the gels is not only determined by the electrostatic effects, hydrophobic interactions also play an important role.

EXPERIMENTAL

Materials

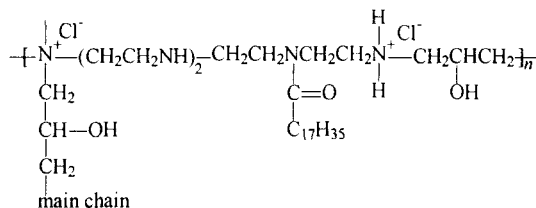
Tetraethylenepentamine (AR) and epichlorohydrin (AR) were distilled before use. Stearic acid, DMSO, acetone, KCl, KI, KBr were used as received.

Synthesis

11.4 g (0.06 mol) of tetraethylenepentamine was dissolved in 15 mL of DMSO in a flask and 6.1 g (0.066 mol) of epichlorohydrin was added dropwise within 1 h under stirring at room temperature. The solution was pre-polymerized for 1 h at 50 °C and polymerized for another 4 h at 95 °C. The polymer was recovered by precipitation in a large amount of acetone and was washed several times with acetone. The polymer was filtered and dried in vacuum overnight at 50 °C (the product designated as PTE).

4.0 g of PTE and 1.0 g of stearic acid were dissolved in 20 mL of DMSO in a flask. The mixture was purged with dried nitrogen gas for at least 30 min to remove oxygen. After the removal of residual oxygen from the reactant mixture, the flask was quickly sealed and the reaction was carried out for 12 h at 120 °C. Hydrophobically modified polymer was recovered by precipitation in a large amount of acetone and was washed several times with acetone. The polymer was filtered and dried in vacuum overnight at 50 °C (the product designated as PTE-C18).

6.22 g of PTE-C18 was dissolved in 18.6 g of distilled water. 1.18 g of epichlorohydrin as a crosslinker was slowly added to the solution with stirring at room temperature. The solution was stirred for another 30 min and 4 mL of 10% KOH solution was then added dropwise to solution. The mixture was poured on a Teflon dish to set a gel slab. The solution gelled after approximately 30 min. On curing for an additional 2 days, the solid polymer slab was gently removed from Teflon dish with a razor blade and soaked in 500 mL of deionized water for 1 week to extract unreacted compounds. The water was replaced daily (the product designated as PTE-C18 hydrogel). Scheme 1 shows the molecular structure of polysoap hydrogel.



Scheme 1

Using the above similar procedure, unmodified hydrophobically poly(tetraethylenepentamine-epichlorohydrin) hydrogels were prepared (the product designated as PTE hydrogel).

Deswelling Experiments

Polysoap hydrogels equilibrated in ionized water were cut into rectangular shaped plates (about 10×10×3 mm). The hydrogel samples were dried for 1 day at room temperature and then for 8 h under vacuum at room temperature. A simulated physiological buffer solution was made according

to the literature^[9]. The buffer solutions with various pH values were prepared by adding 30 wt% of HCl solution.

The dried hydrogels were soaked separately in 50 mL of various buffer solutions with different pH values for 2 days with the solutions being replaced daily with fresh ones. The samples were withdrawn from the buffer solution and the excess surface water was blotted up with tissue paper and then weighted. Deswelling behavior is characterized by the Equilibrium Water Fraction (EWF):

$$EWF = (W_s - W_d) / W_0$$

where W_s is the weight of equilibrium swollen gel in a buffer solution. W_d is the weight of the dried gel. W_0 is the weight of equilibrium swollen gel in deionized water.

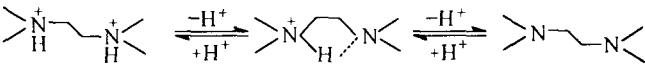
Deswelling kinetics of the gels in buffer solutions with pH value of 8 were examined as follows: the equilibrium swollen gels were soaked in 50 mL of buffer solution. Sample weights were taken at an interval of 10 min as described above.

Deswelling measurements in different ionic species and the strength measurement were taken by soaking the dried gels separately in 50 mL of solutions for 2 days with solution being replaced daily with fresh ones. The sample weights were taken as described above.

RESULTS AND DISCUSSION

As shown in Scheme 1, both the polysoap hydrogel PTE-C18 and polyelectrolyte PTE hydrogel are cationic polyelectrolytes, in which the structure of the polymer main chain affects the pH sensitivity due to the presence of quaternary ammonium and amino groups. The equilibrium degree of deswelling, defined as the weight fraction of water of PTE and PTE-C18 hydrogels in the swollen state, at different pH values are shown in Fig. 1. At $pH < 7$, the deswelling of both polysoap gel and polyelectrolyte gel increases slowly which could be attributed to the effect of ions in buffer solution. When pH value was 8, the water fraction decreased rapidly from ca. 0.98 to ca. 0.2.

Due to the multi-amino monomer units on both polymer main chains, the deswelling behaviour depends mainly on the protonation and deprotonation degree of multi-amino groups in aqueous solution. Scheme 2 shows this process. Before the deprotonation of amino groups at $pH < 7$, there is stronger inter (intra) molecular hydrogen-bond interaction resulting in an expanded conformation of polymer main chains. After deprotonation at $pH > 7$, the hydrogen bond could be disrupted. Both hydrogels experience a conformation transition of polymer main chains from extended coil to compact coil.



Scheme 2

Figure 2 shows the dynamic deswelling expressed as the EWF as a function of the time of immersion of gels in buffer solution at pH 8. It clearly indicates that there is a difference of deswelling rates between PTE and PTE-C18 gels. If a gel is hydrophilic, a repulsive force exists between the segments of the gel. In contrast, hydrophobic interaction acts as an attractive force between the segments. In this case, an abrupt change of deswelling can be enhanced by inter (intra) molecular hydrophobic interaction. Hydrophobic interaction is believed to favor the release of water and deprotonation. On the other hand, Kaneko and co-workers suggested that hydrophilic gel formed “surface skin” layer, entrapping water inside the gel upon the deswelling when they studied a comb-type poly(*N*-isopropylacrylamide)^[10]. Therefore, the deswelling rate of PTE-C18 gel was faster than that of PTE gel.

In general, mobilizable ions inside the gel hardly diffuse out of the gel because of the requirement of maintaining electroneutrality. Therefore, an osmotic pressure exists between solutes inside the gel and solution outside the gel. According to the Donnan equilibrium theory^[11], the concentration of mobilizable ions inside the gel is an important factor for producing the osmotic pressure. When the concentrations of mobilizable ions inside the gel is equal to that outside the gel, an equilibrium deswelling would be attained. If some salts were added into the solution, the concentrations of mobilizable ions outside the gel is higher than that inside the gel, which causes a decrease of osmotic pressure. In this case, the volume of the gel could shrink.

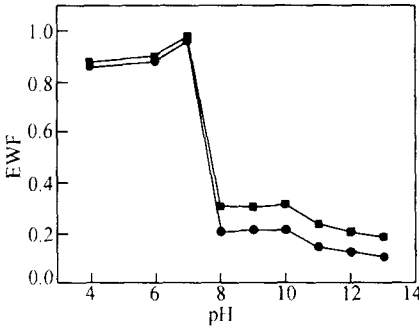


Fig. 1 pH as a function of EWF at 10°C
(■) PTE gel, (●) PTE-C18 gel

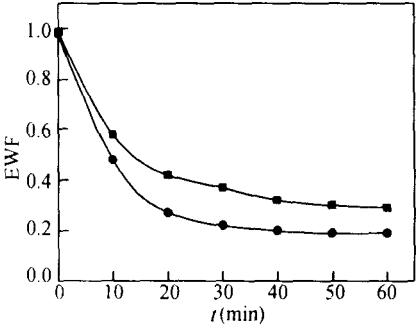


Fig. 2 Time as a function of EWF in buffer solution at pH8
(■) PTE gel, (●) PTE-C18 gel

Figure 3 shows the deswelling behavior of PTE and PTE-C18 in an aqueous electrolyte solution containing Cl⁻ as an ionic species. Obviously, the EWF were effected by the concentration of counterions Cl⁻. The EWF decrease continuously with an increase in the electrolyte concentration and indicate no strong dependence on the cationic species. Generally, the swelling and deswelling of polyelectrolyte gel depends on the association state of ionic groups and affinity of the constituent of gel to solvent. In the case of polysoap gel, hydrophobic interaction is an important factor for the phase transition.

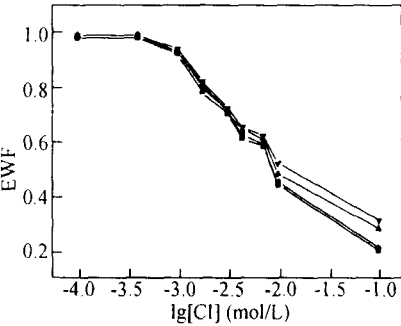


Fig. 3 EWF of gels in NaCl and KCl aqueous solution at 10°C
(▼) PTE—NaCl, (▲)PTE—KCl, (■) PTE-C18—NaCl,
(●) PTE-C18—KCl

As shown in Fig. 4 and Fig. 5, a similar tendency was observed for PTE gel and PTE-C18 gel in aqueous solutions of electrolytes containing different anionic species. A continuous change in deswelling for PTE gel was observed in the KCl, KBr and KI aqueous solutions. In contrast, a discontinuous change was observed in the KI aqueous solution for PTE-C18 gel as shown in Fig. 5. When the concentration of KI increases from 1.0×10^{-3} mol/L to 2.0×10^{-3} mol/L, the EWF

decreases rapidly from 0.86 to 0.58. The PTE and PTE-C18 gels have the same amino groups. The dissociation ability of this ionizable group is considered to be similar for both gels. However, it should be noted that the molecular structure of PTE gel is much less hydrophobic in comparison with PTE-C18 gel.

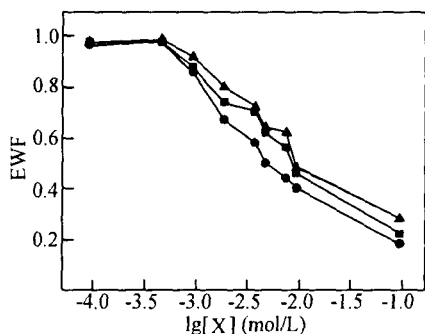


Fig. 4 EWF of PTE gel in various concentration of I^- , Br^- and Cl^- at $10^\circ C$

(Δ) KCl, (■) KBr, (●) KI

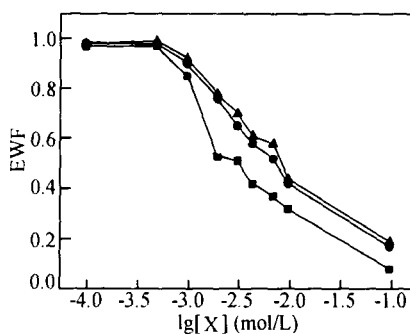


Fig. 5 EWF of PTE-C18 gel in various concentration of KCl, KBr and KI at $10^\circ C$

(Δ) KCl, (●) KBr, (■) KI

Interestingly as shown in Fig. 4 and Fig. 5, the order of effectiveness of the electrolytes that brought about the deswelling of the gels was given as $I^- > Br^- > Cl^-$. This order coincides with that of the association constants of anionic species for quaternary ammonium ion in protonic solvents. These results suggested the importance of the ionic association in transition behavior.

CONCLUSION

The deswelling of PTE and PTE-C18 gels depends on the pH values of buffer solution. A comparison of the deswelling behavior of the PTE gel with that of the PTE-C18 gel verifies the importance of hydrophobic interaction, which enhances the occurrence of the transition. Two important factors, which control the deswelling of PTE and PTE-C18, are deprotonation of amino groups and inter (intra) molecular hydrophobic interaction in aqueous solution. The deswelling of the gels does not depend on the cationic species in the aqueous electrolyte solutions examined but depend strongly on the anionic species. The order of effectiveness of the electrolytes that brought about the deswelling ratio of the gels was given as $I^- > Br^- > Cl^-$. This order coincides with that of the association constants of anionic species for quaternary ammonium ion in protonic solvents.

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