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Swelling Behavior of Hydrophobic Association Hydrogels with High Mechanical Strength

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Hydrophobic association hydrogels (HA-gels) with high mechanical strength, self-healing capability and transparency were successfully prepared by micellar copolymerization, and associated micelles acted as physical crosslinking points in the network structure of HA-gels. In this study, the swelling behavior of HA-gels in distilled water at room temperature was investigated. With increasing the content of hydrophobic monomer in the HA-gels, the swelling degree of HA-gels decreased. According to the results of swelling experiments, a swelling model of HA-gels was proposed, which could reasonably explain the swelling behavior of HA-gels. Moreover, the effect of other test conditions on the swelling behavior of HA-gels was also investigated, such as temperature, sodium dodecyl sulfate (SDS), pH and NaCl. These results indicate that the swelling behavior of HA-gels could be strongly influenced under the conditions mentioned above.

Keywords: Hydrogels, micellar copolymerization, hydrophobic association, swelling behavior

1 Introduction

Hydrogels are three-dimensional network polymers swellable in water and one of the most promising types of polymers being used for new material development. They have attracted considerable attention as special soft and wet materials (1); particularly in biomedical science, where the water imbibing properties of hydrogels enable them to be employed as a potential device for various applications as shown (2–6). The network of hydrogels may be prepared from natural polymer chains or synthetic through chemical or physical cross-links. However, from the viewpoint of materials, the restriction of traditional hydrogels application is mainly because they have serious disadvantages in their mechanical properties as soft materials (7, 8). In addition, for many application fields, the combination of swelling property and good mechanical strength is important (9). The swelling property is one of the most significant properties of hydrogels because it has a profound effect on mechanical properties, permeability, biocompatibility, and surface characteristics (10). Therefore, the design of hydrogels with high mechanical strength and unusual swelling behavior is crucially important in many existing and potential application fields of hydrogels.

Recently, we succeeded in synthesizing a new type of physically crosslinked hydrogels: hydrophobic association hydrogels (HA-gels) with good mechanical strength self-healing capability, and transparency (11, 12). Besides, we also found that HA-gels possessed unusual swelling behavior that has not been reported before. HA-gels were prepared by micellar copolymerization (13–16) of acrylamide (AM) and a small amount of hydrophobic monomer in an aqueous solution containing sodium dodecyl sulfate (SDS), where two kinds of octyl phenol polyethoxy ether acrylates, named as OP-4-AC and OP-10-AC respectively, acted as hydrophobic monomers. Therefore, HA-gels were composed of hydrophobically modified polyacrylamide (HM-PAM), SDS and water. Miquelard-Garnier et al. (17) prepared a hydrophobically modified hydrogel where the hydrophobic groups in the gel could self-assemble to form micelles. Similarly, within HA-gels, a large number of associated micelles were formed by hydrophobic association of SDS and hydrophobic groups belonging to two or more HMPAM chains. Such associated micelles acted as effective cross-linkers. Consequently, the three-dimensional network of HA-gels could be constructed. We proposed the structural model for HA-gels depicted in Figure 1 (12). As a result of the unique network structure, HA-gels are attractive for a wide range of applications.

The construction, the self-healing mechanism and the mechanical behavior of HA-gels were discussed in detail elsewhere (11, 12). These results showed HA-gels possessed

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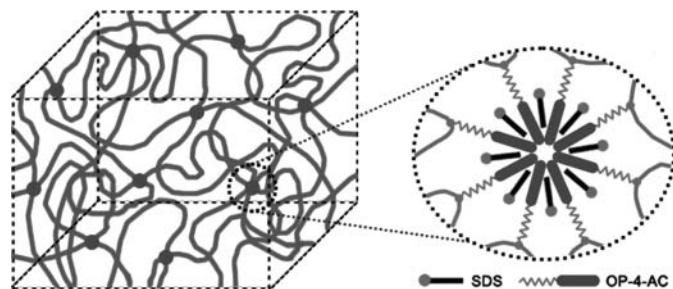


Fig. 1. Schematic illustration of the structural model with associating networks in the HA-gels, which consists of associated micelles and flexible polymer chains connected by neighboring associated micelles. For simplicity, only a small number of polymer chains are described in the structural model.

the unique network structure and their mechanical properties strongly depended on the content of compositions in the initial reaction solution, and they exhibited high recovery even after extensive elongations and obvious thermoelastic behavior. HA-gels with variously available properties, such as the thermoresponsive HA-ge, the nano-spheres composite HA-gel and the fluorescent HA-ge were also reported. Here, the origin of the swelling behavior of HA-gels and the effect of different variables on their swelling behavior are discussed on the basis of the results of the swelling tests in detail.

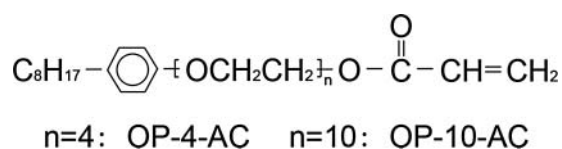
2 Experimental

2.1 Materials

OP-10-AC and OP-4-AC was prepared according to the synthetic procedure reported previously (11) and their chemical structure is given in Scheme 1. AM and potassium persulfate (KPS) were purchased from Tianjin Fuchen Chemical Reagent Factory, China. Other reagents were purchased from Beijing Chemical Works, China. All these reagents were used as received except AM and KPS which were recrystallized from distilled water before use and dried under vacuum at room temperature.

2.2 Synthesis of HA-gels

The synthetic procedure of HA-gels is the same as that reported previously (11). In order to prepare various HA-gels with different compositions, the hydrophobic monomer content in the initial solution were varied over a wide range. In the present study, HA-gels containing OP-4-AC or OP-



Sch. 1. Chemical structure of the hydrophobic monomers used in the text.

10-AC are expressed as F-OP4-X% gels or T-OP10-X% gels, where X stands for molar percentage of OP-4-AC or OP-10-AC relative to AM in the initial reaction solution and weight concentrations of SDS and AM were 3 wt% and 10 wt%, respectively. All the total mass of the initial reaction solution was 60.00 g. Nomenclature and the content of compositions in the initial reaction solution for F-OP4-X% gels and T-OP10-X% gels are listed in Table 1. For example, the experimental procedure used for F-OP4-3% gel was as follows: first, a transparent aqueous solution consisting of AM (6.00 g), OP-4-AC (1.11 g), SDS (1.80 g), and distilled water (47.53 g) were prepared. Then, the aqueous solution of initiator (KPS 0.0356 g in water 3.56 mL) was added to the former solution. Next, the solution was added to a test tube containing round plastic molds and drove out dissolved oxygen with N_2 for 10 min under normal pressure, and then the tube was sealed. After being placed at room temperature for 1 h, micellar copolymerization was carried out in a water bath at 50°C for 5 h. As a result, F-OP4-3% gel was prepared.

2.3 Swelling Behavior

2.3.1. Swelling Behavior of HA-gels in Distilled Water at Room Temperature

Swelling experiments were performed by immersing as-prepared F-OP4-X% gels and T-OP10-X% gels (initial size of 7 mm diameter \times 5 mm length) in a large excess of distilled water at room temperature and distilled water was replaced every day. In each measurement, the samples were removed from distilled water and weighed after removing excess distilled water from their face, and then these samples were dried to constant weight in oven at 70°C . The swelling degree was expressed by the ratio of the weight of the swollen hydrogel to its corresponding dried gel weight, and the gel fraction was expressed by the ratio of the dried gel weight after a certain swelling time to its theoretical dried gel weight. Here, the theoretical dried gel weight means theoretical solid weight based on the experimental recipe.

2.3.2. Swelling Behavior of HA-gels Under Other Test Conditions

Swelling experiments were performed by immersing as-prepared F-OP4-1% gel (initial size of 7 mm diameter \times 5 mm length) in an excess of immersing liquid. Swelling behavior of HA-gels was obtained under the following conditions respectively: different temperature (immersing liquid: distilled water); different weight concentration SDS solutions room temperature); different pH solutions room temperature); different weight concentration NaCl solutions (room temperature) Then, after a certain time interval, the samples were took about 10 s from the immersing liquid and weighed after removing excess immersing liquid from their face; they were still placed in the immersing

Table 1. Nomenclature and the content of compositions in initial reaction solution for HA-gels

HA-gels	AM (g)	OP-4-AC (g)	OP-10-AC (g)	SDS (g)	KPS ^a (mL)	H ₂ O (g)
F-OP4-1%	6.00	0.37	—	1.80	3.19	48.64
F-OP4-2%	6.00	0.74	—	1.80	3.37	48.09
F-OP4-3%	6.00	1.11	—	1.80	3.56	47.53
F-OP4-5%	6.00	1.84	—	1.80	3.92	46.44
T-OP10-1%	6.00	—	0.59	1.80	3.30	48.31
T-OP10-2%	6.00	—	1.18	1.80	3.59	47.43

^aConcentration of KPS was 0.01g/mL.

liquid after weighing. Swelling degree was expressed by the ratio of the weight of the swollen hydrogel to its theoretical dried gel weight.

3 Results and Discussion

3.1 Swelling Behavior of HA-gels in Distilled Water at Room Temperature

Hydrogels swell or shrink in aqueous solutions due to the association, disassociation and binding of various ions to polymer chains (18), and the swelling property is one of the most important parameters to evaluate hydrogels. Figure 2 shows the swelling degree and the gel fraction of F-OP4-X% gel samples as a function of swelling time in distilled water at room temperature. During the course of swelling test, no distortion in the cylindrical shape of hydrogels was observed for all F-OP4-X% gel samples. It is seen that the

swelling degree of F-OP4-X% gels rapidly increased with increasing swelling time and attained a maximum value after about one day. Surprisingly, a further increase in swelling time resulted in the deswelling of the hydrogels until they began swelling up and down about a certain swelling degree. Then, with increasing swelling time, the swelling degree of F-OP4-1% gel, F-OP4-2% gel and F-OP4-3% gel increased and the swelling degree of F-OP4-5% gel was basically unchanged. In the swelling process, with changes in the swelling degree, the gel fraction of F-OP4-1% gel, F-OP4-2% gel and F-OP4-3% gel first unchanged and then decreased; however the gel fraction of F-OP4-5% gel remained approximately constant.

The unusual swelling behavior of HA-gels has not been reported before. To understand the origin of the swelling behavior of HA-gels, we propose a swelling model of HA-gels on the basis of the experimental results. As shown in Figure 3, we believe that the swelling process of

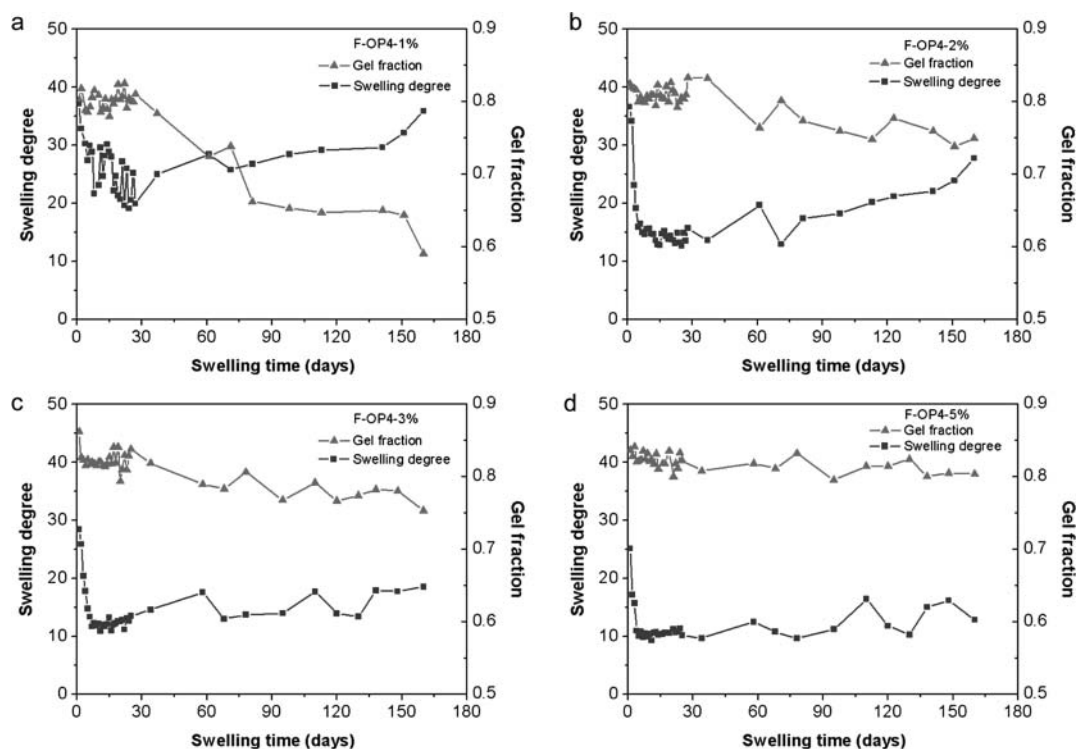


Fig. 2. Swelling degree and gel fraction of F-OP4-X% gel samples as a function of swelling time in distilled water at room temperature, (a) F-OP4-1% gel, (b) F-OP4-2% gel, (c) F-OP4-3% gel, and (d) F-OP4-5% gel.

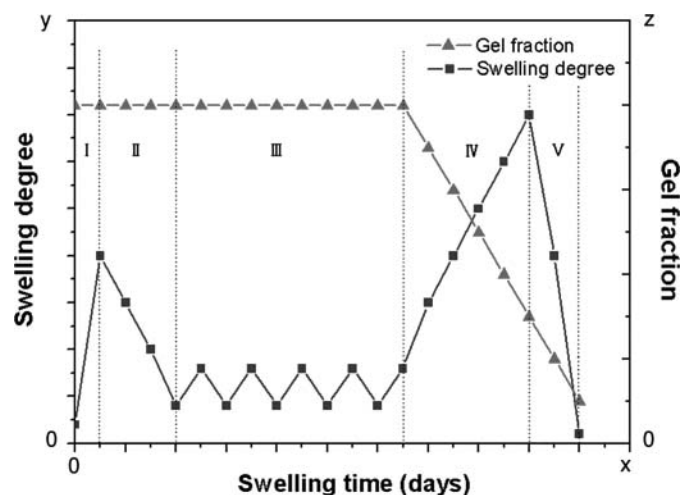


Fig. 3. Schematic representation of the swelling process of HA-gels. (I) over-swelling, (II) self-deswelling, (III) dynamic equilibrium of disassociation and re-association, (IV) disassociation enjoying the advantage, and (V) dissolution. x indicates the value of swelling time, y indicates the value of swelling degree, and z indicates the value of gel fraction ($z \leq 1$).

HA-gels can be divided into five stages: over-swelling (I), self-deswelling (II), dynamic equilibrium of disassociation and re-association (III), disassociation enjoying the advantage (IV) and dissolution (V). For the first stage, the swelling degree increases rapidly and the gel fraction is unchanged with increasing swelling time. This is because the solvent molecules penetrate into HA-gels and therefore the volume of HA-gels undergoes rapid expansion, HMPAM molecules in HA-gels do not enter into the solvent and therefore the gel fraction is constant. It should be indicated that some sols in hydrogel sample would

be extracted at the beginning of swelling process, which would result in decreasing the gel fraction, see Figure 2. This change in the gel fraction, however, was not reflected in the swelling model proposed in order to facilitate discussion. In addition, the first stage mentioned above was accomplished after about one day, so it could not be showed clearly on the swelling curves with the time scale showed in Figure 2. This stage will be clearly displayed in the followed section, in which the time interval between two weighting for the swollen sample is enough short.

For the second stage of swelling, the swelling degree decreases with increasing swelling time, which indicates that the network structure of HA-gels was already changed. We think that this self-deswelling behavior of HA-gels is mainly owed to the rearrangement of their associated micelles, which means that some weak associated micelles disassociated at first stage will re-form strong associated micelles on their own or with other associated micelles during the course of swelling, see Figure 4.

For the third stage, the swelling degree begins swelling up and down at a certain swelling degree with an increasing swelling time, which results from the dynamic equilibrium process of disassociation and re-association of associated micelles in HA-gels. Similar to the first stage, the gel fraction of the second stage and the third stage is also unchanged. Incidentally, it should be pointed out that the room temperature fluctuations also affected the dynamic equilibrium process of disassociation and re-association of associated micelles, which would only affect the testing results, but made no impression on the phenomenon of swelling fluctuations; when the swelling tests were made within a relative narrow range of time, this effect could be ignored.

For the fourth stage, the swelling degree began to increase monotonously, which is due to the disassociation

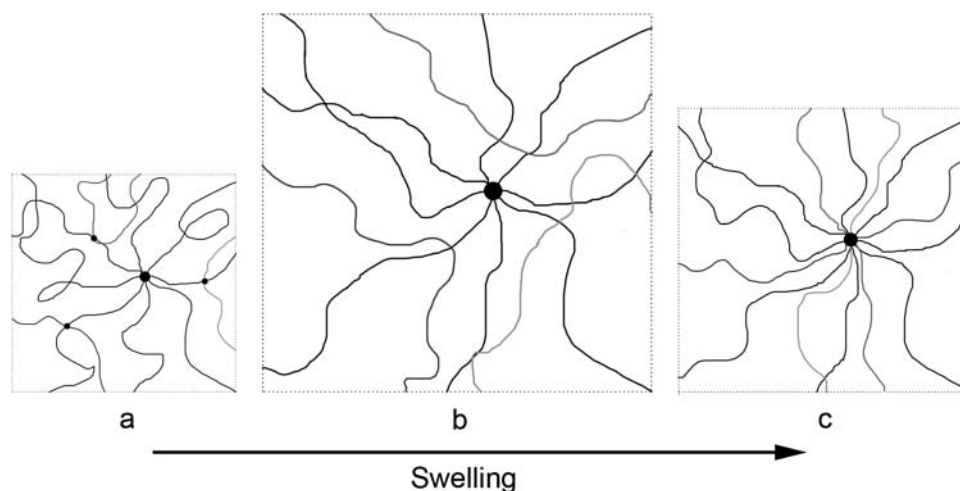


Fig. 4. Schematic diagram of self-deswelling behavior of HA-gels. Color lines indicate HMPAM chains with weak associated micelles, the small black solid circle indicates weak associated micelles, and the big black solid circle indicates strong associated micelles. Only a part of HA-gels is drawn for clarity.

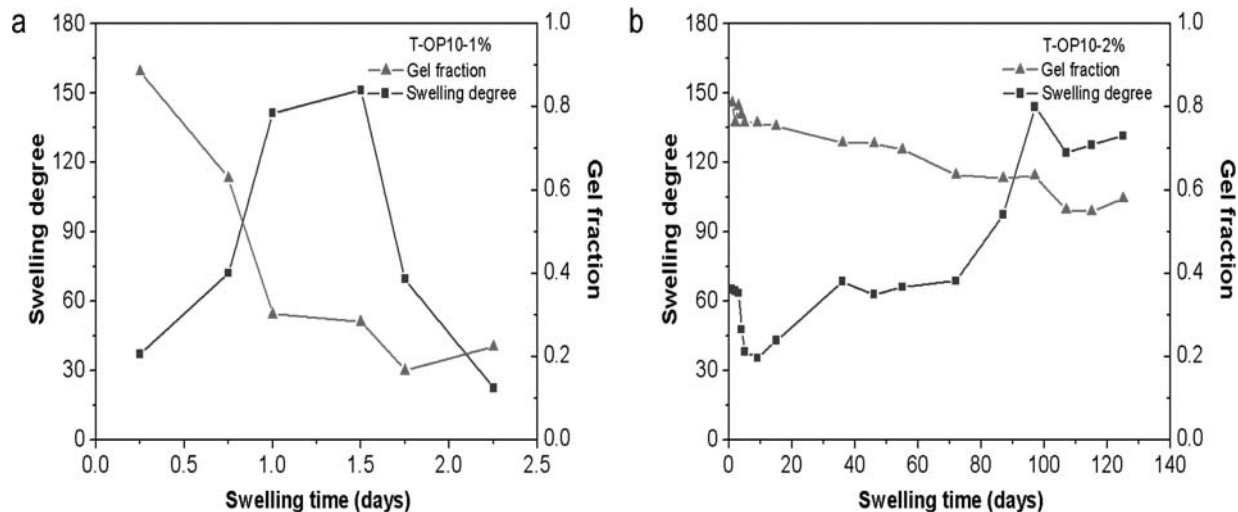


Fig. 5. Swelling degree and gel fraction of T-OP10-X% gel samples as a function of swelling time in distilled water at room temperature, (a) T-OP10-1% gel and (b) T-OP10-2% gel.

behavior of HA-gels beginning to benefit from the advantage relative to the re-association behavior and the number of associated micelles in HA-gels decreases gradually with increasing swelling time. If there is a further increase in swelling time, the swelling behavior of HA-gels enters into the fifth stage, namely the stage of dissolution, which is because there is only the disassociation behavior for HA-gels. With the benefit of the advantage for the disassociation behavior of HA-gels, HMPAM molecules in HA-gels begin to enter into the immersing liquid, therefore, the gel fraction of the fourth stage and the fifth stage decreases with increasing swelling time.

However, for F-OP4-X% gels, the fifth stage of swelling process of HA-gels was not observed, see Figure 2. This is because the dissolution of HA-gels prepared by OP-4-AC requires a considerable length of swelling time owing to strong hydrophobic property of OP-4-AC. To verify the fifth stage, we also tested the swelling behavior of T-OP10-X% gels in which hydrophobic monomer was OP-10-AC, see Figure 5. In Figure 5a, the swelling behavior of T-OP10-1% gel first increased and then decreased while its gel fraction decreased monotonously, which was different from the above swelling model of HA-gels. There are two possible reasons for the phenomenon: hydrophobic property of OP-10-AC is weaker than that of OP-4-AC; another reason is that the content of hydrophobic monomer for T-OP10-1% gel was low. In Figure 5b, the swelling behavior of T-OP10-2% gel was basically consistent with the swelling model. The third stage of swelling process for T-OP10-2% gel was shortened because the backbone chains was endowed with more moving freedom due to a longer distance between the hydrophobic group and backbone for OP-10-AC type HA-gels, and the fifth stage was not be evidenced because the swelling time was inadequate.

3.2 Effect of the Other Test Conditions on Swelling Behavior of HA-gels

3.2.1. Effect of Temperature on Swelling Behavior

Hydrophobic association is a non-covalent bond and reversible, so it will be disassociated at high temperature. For HMPAM aqueous solutions, McCormick et al. (19) pointed out that the interchain hydrophobic association of HMPAM is favored by increasing the temperature, at least to an extent. However, at a higher temperature, the hydrophobic association decreases because of the faster movement of water molecules and polymer chains (20). For a crosslinked network structure of hydrogels, with increasing temperature, chain segment motion speed up, and the role played by polymer chain on crosslinking points will also be enhanced. Moreover, experiments showed that the tensile stress increased linearly with the increasing temperature (12). That is, for HA-gels, the higher the temperature, the greater the tensile stress, and so the greater the disassociation driving force. Therefore, temperature will have an impact on disassociation, as well as the swelling behavior of HA-gels.

Figure 6 shows the swelling degree of F-OP4-1% gel as a function of swelling time in distilled water at a different temperature. We observed that the temperature had a strong impact on the swelling behavior of HA-gels. At the same swelling time, the swelling degree increased with increasing temperature, which shows that higher temperature would promote the disassociation of their associated micelles. When the temperature was 50°C and 80°C, the swelling behavior of F-OP4-1% gel did not exhibit the phenomenon of self-deswelling and the hydrogel samples dissolved in a relatively short period of swelling time, which indicates that the re-association of free hydrophobic groups did not happen at the higher temperature.

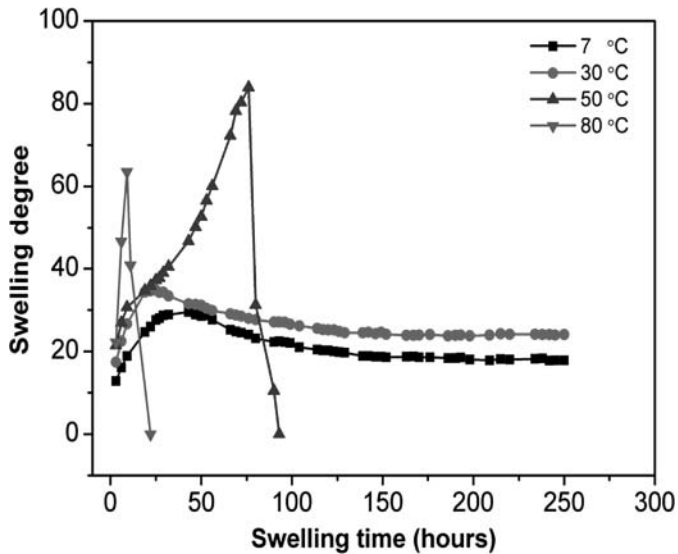


Fig. 6. The effect of temperature on swelling behavior of HA-gels in distilled water. Hydrogel sample: F-OP4-1% gel.

3.2.2. Effect of SDS on Swelling Behavior

A hydrogel with mechanical strength is both concentrated polymer solution and highly elastic solid, so small molecules can penetrate or spread into the hydrogel. Therefore, during the course of the swelling test, small molecules can penetrate into HA-gels due to the osmotic pressure between the hydrogel and immersing liquid. It is the main reason for the penetration phenomenon, which is a different chemical potential exists between a solvent of solution and pure solvent. The chemical potential of an aqueous solution containing SDS (immersing liquid), μ_n (all n in this section stands for SDS weight concentration of the immersing liquid, namely n wt%, $n = 0, 3$ and 10 , respectively), was calculated as follows:

$$\mu_n = \mu^{0(g)} + RT \ln p_n \quad (1)$$

Where $\mu^{0(g)}$ is the chemical potential of distilled water, p_n is saturated vapor pressure of an aqueous solution containing SDS, R is gas constant, and T is the absolute temperature. According to Raoult's law, the descending order of value of p_n is: p_0, p_3 and p_{10} . Therefore, the value of μ_n in the descending order is: μ_0, μ_3 and μ_{10} . Because the hydrogel is concentrated polymer solution, the chemical potential of F-OP4-1% gel, which is the sample of swelling test in the immersing liquid containing different weight concentrations of SDS, can be expressed as μ_{gel} . The chemical potential difference between the immersing liquid and the sample of hydrogel, $\Delta\mu_n$, can be calculated via:

$$\Delta\mu_n = \mu_n - \mu_{gel} \quad (2)$$

According to the above discussion, we know the value of $\Delta\mu_n$ in the descending order is: $\Delta\mu_0, \Delta\mu_3$ and $\Delta\mu_{10}$. Therefore, in the immersing liquid containing different SDS

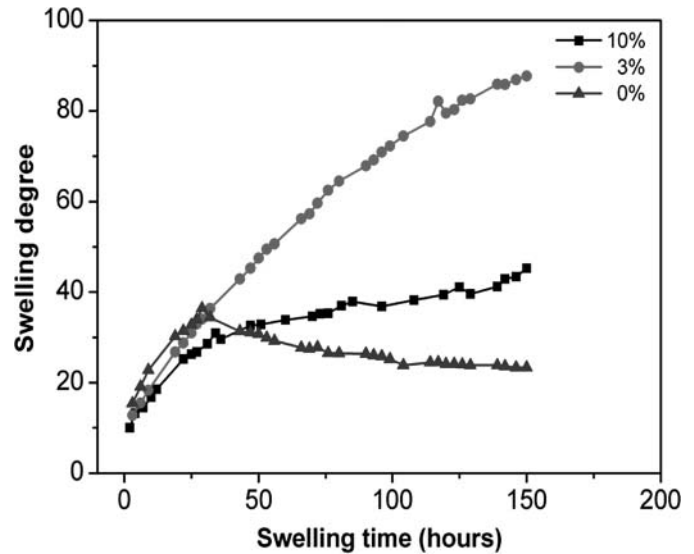


Fig. 7. The effect of SDS on swelling behavior of HA-gels at room temperature. Hydrogel sample: F-OP4-1% gel. The percent in figure stands for weight concentration of SDS.

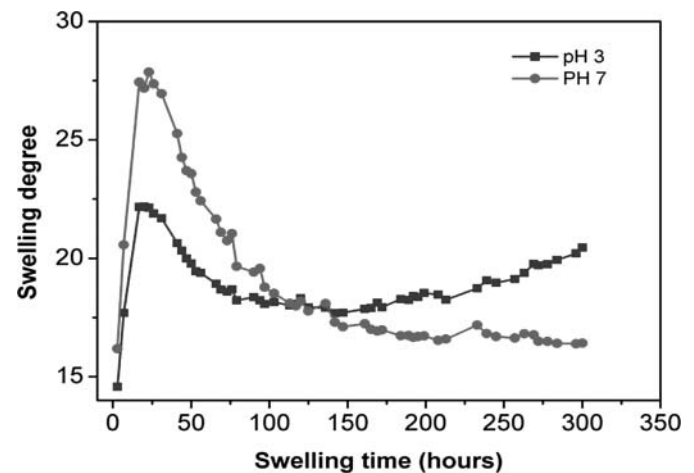


Fig. 8. The effect of pH on swelling behavior of HA-gels at room temperature. Hydrogel sample: F-OP4-1% gel.

weight concentrations, the descending order of the value of the osmotic pressure Π_n between immersing liquid and the sample of hydrogel is: Π_0, Π_3 and Π_{10} . As a result, it is predicated that the swelling degree of HA-gels will decrease with an increasing SDS concentration of the immersing liquid.

On the other hand, the SDS entered into HA-gels from the immersing liquid will tend to associate with hydrophobic groups (21). The role of SDS is twofold: first, to prevent the transition from weak associated micelles to the strong associated micelles; second, to prompt the dissociation of the strong associated micelles. Therefore, the hydrogel samples in the immersing liquid containing SDS will continuously swell with increasing swelling time.

Figure 7 shows the swelling degree of F-OP4-1% gel as a function of swelling time in SDS solution with different weight concentrations at room temperature. It can be seen that the swelling degree of the sample in the immersing liquid containing 10 wt% SDS is lower than that in the immersing liquid containing 3 wt% SDS, and the swelling degree of the sample in the immersing liquid containing 0 wt% SDS (distilled water) at the beginning stage is larger than that in the immersing liquid containing 3 or 10 wt% SDS, which suggests that the osmotic pressure difference between hydrogel and aqueous phases should be the main reason for this phenomenon. In addition, after about 29 h, the sample in distilled water exhibited the phenomenon of self-deswelling, while the others continually swelled. Because the weight concentration of SDS for the sample of F-OP4-1% gel was 3 wt% (Table 1), free SDS molecules could not exude through the hydrogel in the immersing liquid containing 3 or 10 wt% SDS. The superfluous SDS molecules in the hydrogel samples would prompt the disassociation of their associated micelles and inhibit its re-association, which is the main reason that the sample of F-OP4-1% gel in the immersing liquid containing 3 and 10 wt% SDS to continually swell and did not show any self-deswelling phenomenon.

3.2.3. Effect of pH on Swelling Behavior

The swelling behavior of F-OP4-1% gel was studied at various pH values (pH 3, pH 7 and pH 13) at room temperature, (Fig. 8). To prepare the immersing liquids, standard HCl (pH 1) and NaOH (pH 13) solutions were diluted with distilled water to reach the desired pH value, respectively. The sample of F-OP4-1% gel completely dissolved in the immersing liquid of pH 13 within 3 h, therefore, the curve of its swelling degree did not appear in Figure 8. For the immersing liquids of pH 3 and pH 7, the swelling behavior of F-OP4-1% gel was consistent with the swelling model mentioned above. However, the third stage of the swelling process of F-OP4-1% gel in the immersing liquid of pH 3, the dynamic equilibrium of disassociation and re-association, was much shorter than that in the immersing liquid of pH 7.

Partial hydrolysis of the water-soluble acrylamide blocks of the copolymers leads to an increased solubility of the copolymers and a consequent decrease in the numbers of hydrophobic liaisons (22). Furthermore, it is known that hydrolyzed samples can be obtained from acidic or alkaline hydrolysis of polyacrylamide (23). Therefore, the phenomenon mentioned above can be attributed to hydrolysis of acrylamide units in HMPAM. Under alkaline conditions, the alkaline hydrolysis of amides in acrylamide units proceeds as a first order reaction with respect both to amide and to hydroxyl ions (24), which lead to completely dissolution of F-OP4-1% gel in the immersing liquid of pH 13 within a short time. Similar to alkaline hydrolysis, the acrylamide units in HMPAM can also hydrolyze under acid conditions although the reaction proceeds slowly in

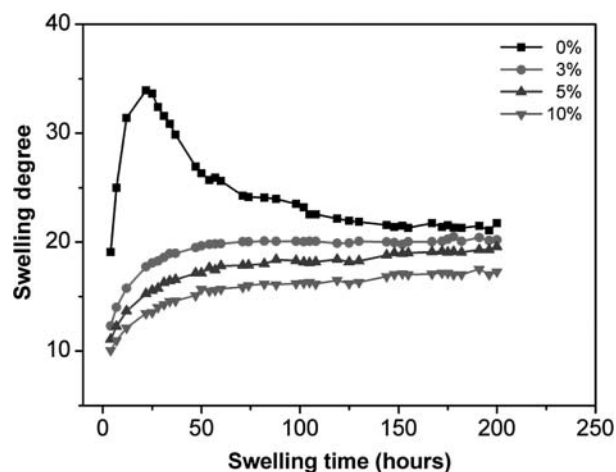


Fig. 9. The effect of NaCl on swelling behavior of HA-gels at room temperature. Hydrogel sample: F-OP4-1% gel. The percent in figure stands for weight concentration of NaCl.

slightly acidic medium (23). Consequently, due to the effect of acid hydrolysis, the period of the third stage of the swelling for F-OP4-1% gel in the immersing liquid of pH 3 was greatly reduced. The swelling degree of F-OP4-1% gel in the immersing liquid of pH 7 was higher than that in the immersing liquid of pH 3 at the first and the second stage of swelling process, which maybe owe to the osmotic press effect mentioned above. However, no direct data have been determined here to prove that the acrylamide units have hydrolyzed, so the effect of pH on swelling behavior of HA-gels still remains a hypothesis, and the detailed investigation is in progress.

3.2.4. Effect of NaCl on Swelling Behavior

Figure 9 shows the swelling degree of F-OP4-1% gel as a function of swelling time in different weight concentration NaCl solutions at room temperature. During the course of the swelling test, all samples in the immersing liquid containing NaCl exhibited the phenomenon of phase separation. The swelling degree of the hydrogel sample decreased with increasing the concentration of NaCl. In addition, it should be noted that the second stage of the swelling, i.e., self-deswelling, disappeared for F-OP4-1% gel in the immersing liquid containing NaCl.

The effect of salt on hydrophobic association of HMPAM has been investigated for several decades and extensively documented (19, 20, 25, 26). Effing et al. (25) have reported evidence for an associative phase separation in a mixture of HMPAM and SDS induced by the presence of salt. During the course of the swelling test, NaCl molecules can penetrate into hydrogel because of the osmotic press between the hydrogel sample and the immersing liquid, which must affect the swelling behavior of HA-gels. The salting-out effect as a driving force for phase separation can promote the extent and strength of hydrophobic association of HA-gels. In addition, because of the osmotic

pressure effect, the amounts of water absorbed by hydrogel will decrease significantly under the condition of immersing liquid containing salt (27). For these reasons, the presence of salt seriously reduced the swelling degree of HA-gels. Moreover, because the salting-out effect can change weak hydrophobic association to strong hydrophobic association, the rearrangement of associated micelles in F-OP4-1% gel was suppressed, which directly led to the disappearance of the second stage of swelling for F-OP4-1% gel in NaCl solutions.

4 Conclusions

The main purpose of this study was to investigate the swelling behavior of HA-gels. The swelling process of HA-gels can be divided into five stages: over-swelling (I), self-deswelling (II), dynamic equilibrium of disassociation and re-association (III), disassociation enjoying the advantage (IV) and dissolution (V). It should be noted that the five stages may not be completely exhibited under the special conditions, such as lower hydrophobic monomer content, high temperature, and strong alkaline solutions. Although the complete swelling process of F-OP4-X% gels was not directly observed because the required immersing time was too long, the existence of the fifth stage of swelling process for HA-gels could be verified from the swelling behavior of T-OP10-1% gel. For F-OP4-X% gels, their swelling degree decreased with increasing hydrophobic monomer content. With increasing temperature, the swelling degree of F-OP4-1% gel increased and its swelling process was dramatically reduced at 50°C and 80°C. Under the conditions of the immersing liquid containing different SDS concentrations at room temperature, with increasing SDS content, the swelling degree of F-OP4-1% gel decreased due to the osmotic pressure difference between the hydrogel and the immersing liquid, and the hydrogel self-deswelling behavior did not show in the immersing liquid containing 3 wt% and 10 wt% SDS. The swelling behavior of HA-gels was strongly influenced by pH value of the immersing liquid due to the hydrolysis effect of acrylamide units in HMPAM. The sample of F-OP4-1% gel completely dissolved in the immersing liquid of pH 13 within 3 h; for the immersing liquids of pH 3 and pH 7, the swelling process of F-OP4-1% gel exhibited the self-deswelling behavior; for the immersing liquid of pH 3, the third stage of swelling process was reduced. Moreover, the swelling behavior of HA-gels in the immersing liquid containing NaCl was also investigated. Because of the salt-out effect and the osmotic pressure difference between the hydrogel and the immersing liquid, the swelling degree of F-OP4-1% gel decreased with increasing NaCl content of the immersing liquid, and the hydrogel self-deswelling behavior did not appear in NaCl solutions.

From what has been discussed above, we may safely draw the conclusion that the life of HA-gels in the immersing liquid, which starts on the beginning of swelling test and ends

on the beginning of the fifth stage of swelling process, can be adjusted in accordance with application requirements by changing the hydrogel chemical structure (the type and amount of hydrophobic monomer) and the immersion environment. Therefore, we are sure that HA-gels will be widely used in various fields due to high mechanical strength and unusual swelling behavior.

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