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Radiation synthesis and characterization of polyacrylic acid hydrogels

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Abstract The pH-sensitive polyacrylic acid (PAA) hydrogels were synthesized by gamma-ray irradiation at an ambient temperature. The influences of dose, monomer concentration, cross-linking agent content, pH, and ionic strength on the swelling ratio (*SR*) of the PAA hydrogels were investigated in detail. The results show that the *SR* of the hydrogel decreases with an increase in the dose, monomer concentration, and cross-linking agent content. In alkaline solution, the *SR* of the hydrogels is much higher than that in acid solution. Also, the ionic strength can influence the *SR* of the hydrogels. The more the concentration, the lower the *SR*.

Keywords pH-sensitive behavior, Polyacrylic acid hydrogels, Radiation synthesis

CLC numbers O644, O631

1 Introduction

Stimuli-responsive hydrogels are crosslinked hydrophilic polymeric networks that exhibit various swelling properties depending on environment variables such as pH, temperature, ionic strength, and electric field.[1-2] Such hydrogels are used for biomedical purposes. They are mainly applied to wound dressing, drug delivery systems, dental applications, injectable polymers, implants, and ophthalmic applications.[3] Since Tanaka discovered that the polyacryamide hydrogels exhibit a pH-sensitive behavior in the late 70's of the twentieth century,[4] the pH-sensitive hydrogels have attracted great interest. They have been investigated extensively in recent years because of their pH-sensitive, hydrophilic character, and potential applications. More specifically, the pH-sensitive hydrogels have been frequently used in sustained gastro-intestinal drug delivery systems.[5]

Because of the presence of carboxylic acid side groups, the swelling behavior of the polyacrylic acid (PAA) hydrogels is highly dependent on the pH of the surrounding medium.[6] So, the PAA hydrogels exhibit a better pH-sensitive behavior and potential applications. However, the poor mechanical property of the PAA hydrogels prepared with the chemical initiation method is a limiting factor for several applications.[7] In recent years, considerable researches have been made on the characterization and swelling behavior of copolymer hydrogels and interpenetrating polymer network hydrogels prepared with acrylic acid monomers and other monomers.[8,9]

Radiation polymerization has many advantages over other conventional methods. No catalysts or additives are needed to initiate the reaction. Physical properties can be easily controled by combining absorbed dose with polymer composition. Especially, if combined with simultaneous sterilization of the product, radiation is a very convenient tool for the synthesis of hydrogels.[10]

In this article, the PAA hydrogels were synthesized by gamma-ray irradiation, and some of their properties were investigated.

2 Experimental

2.1 Materials

Acrylic acid (AAc) monomer and cross-link

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agent N,N'-methylenebisacrylamide (MBA) were purchased from Zhengzhou Zhongliang Chemical Co., China. They were used to prepare the hydrogels without any further purification. Water was triple distilled. Other agents, all A. R. grade, were used without treatment.

2.2 Preparation of PAA hydrogels

The prepared AAc monomer solutions with a certain MBA content, as a crossing agent, were transferred into glass tubes of 10 mm diameter, bubbled with N_2 for 10 min, and then the tubes were sealed. The synthesis of the hydrogels in the aqueous solution was carried out under irradiation of γ-rays from a ^{60}Co source at room temperature, with the absorbed doses between 10 and 22 kGy. The hydrogels obtained in long cylindrical shape were cut into pieces of 2-3 mm and dried in vacuum at 50℃ to constant weight. The dried gels obtained were stored in a drying apparatus for later evaluation.

2.3 Swelling behavior of PAA hydrogels

For measurement of the swelling ratio (*SR*), the weighted dry gels were immersed in a beaker filled with distilled water at 25℃. The weight of swollen sample was measured at various time intervals after excess surface water was removed using filter paper. The procedure was repeated until there was no further weight increase. The *SR* of the hydrogels can be calculated as follows:

$$SR = (W_s - W_d)/W_d \quad (1)$$

where W_d is the initial weight of the dry gel and W_s is the weight of the swollen hydrogels at different times.

Influence of some factors such as pH, temperature as well as inorganic salt concentration on the swelling behavior of the hydrogels was also studied by determining the *SR* at the above-mentioned condition for 24 h. The buffer solutions with various pH values were prepared according to Ref.[11].

3 Results and discussion

3.1 Swelling properties of PAA hydrogels

Fig.1 shows the swelling kinetics and time dependent swelling behavior of the hydrogels prepared at doses of 14 kGy, 18 kGy and 22 kGy, respectively. It can be found that the *SR* of these hydrogels is very high at the beginning, and after 13 h, the hydrogels basically reach the equilibrium of swelling. These results can be explained as follows: when the dried PAA gels are immersed in distilled water at 25℃, the intermolecular hydrogen bonding can be built between the carboxylic acid group and water molecule because the carboxylic acid side group has good hydrophilicity. Water molecules can easily permeate through the gel networks in hydrogels, which results in the hydrogels swelling. As the swelling time increases, the hydrogels contain a large amount of water, which results in the hydrogel network growing and the elastic restoring force of network increasing, so the *SR* of the PAA hydrogels will finally reach a certain amount. It can also be found that the equilibrium *SR* of the PAA hydrogels decreases with an increase in the total absorbed dose. This can be explained in terms of the crosslinking degree, which increases with an increase in the total absorbed dose. The increment in the degree of crosslinking reduces the free volume available for swelling by increasing the tightness of the network structure. Highly crosslinked hydrogels have a tighter structure and less *SR* compared to the hydrogels with lower crosslinking ratios. Crosslinking hinders the mobility of the polymer chain, and hence lowers the *SR*. As the absorbed dose increases, more polymer chain radicals are produced, so the crosslink density of the gel network increases because of the termination reaction of the polymer chain radicals.

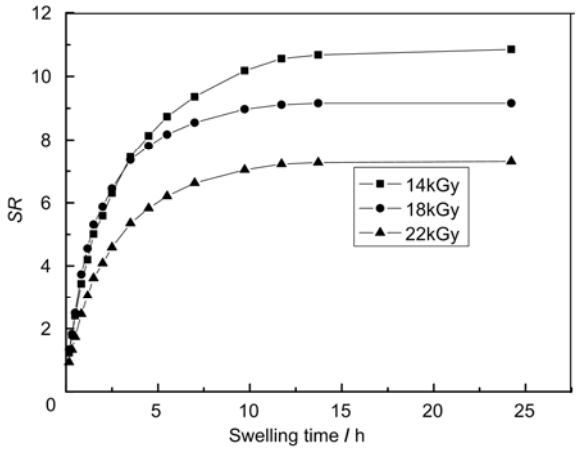

Fig.1 The *SR* of the PAA hydrogels prepared at different absorbed doses versus swelling time.

Fig.2 shows the effect of temperature on the *SR* of the hydrogels prepared at several different mono-

mer concentrations. When the mass concentration of monomer is changed from 7% to 15%, the *SR* of the hydrogels decreases with an increase in the monomer concentration. This is because a higher AAc concentration results in a larger tangle between the molecular chains of the hydrogels. To a certain extent, the tangled molecular chain has the same influence on the *SR* of the hydrogels with the crosslinked network, therefore the *SR* of the hydrogels decreases.

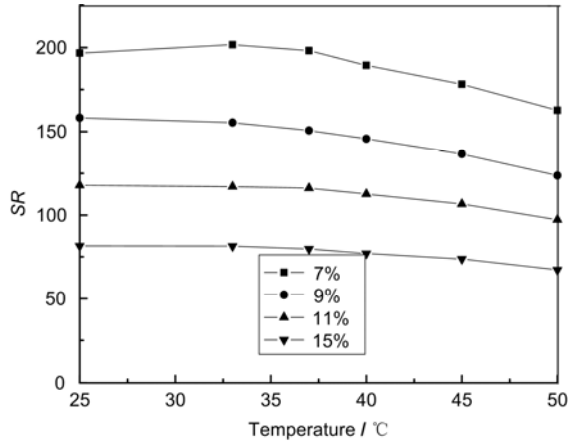

Fig.2 The *SR* of the PAA hydrogels prepared at different mass concentrations of monomer as a function of temperature.

At a higher temperature range, the *SR* of the hydrogels decreases with the increase in temperature of hydrogels in the swollen state. This phenomenon can be explained as a higher temperature results in lower osmotic pressure because of the higher speed of water molecular motion and thus a lower *SR*.

Fig.3 shows the change of *SR* of the hydrogel immersed into the KCl solutions with various concentrations after the sample had swollen in distilled water

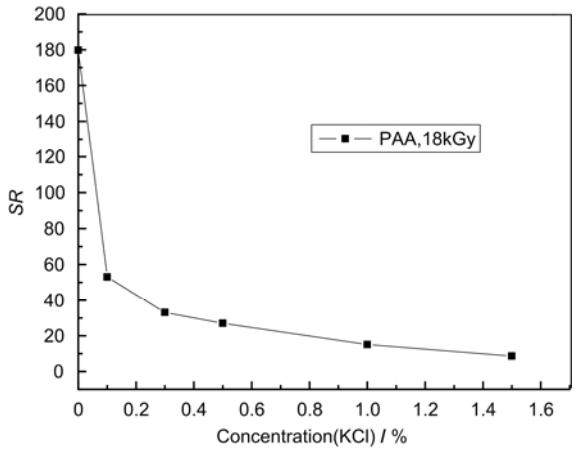

Fig.3 Effect of the concentration of KCl solutions on the *SR* of the PAA hydrogels at 25℃.

at 25℃. With the increase of the KCl solution concentration, the *SR* of the hydrogel decreases and the volume of the hydrogel shrinks. This phenomenon may be attributed to a large amount of water entering into the medium from the hydrogel network as a result of the water losing its osmotic balanced state.

3.2 pH-sensitive PAA hydrogels

Fig.4 shows the effects of contents of the crosslinking agent and pH on the *SR* of the hydrogels. It can be found that the *SR* of the hydrogels decreases with increasing content of the crosslinking agent, especially in alkaline buffer solutions. It can be explained that crosslink density of the gel network increases because of an increase in the MBA content. The increase of crosslink density results in the decrease of the *SR* and the increase of hydrophobicity of the gel network.

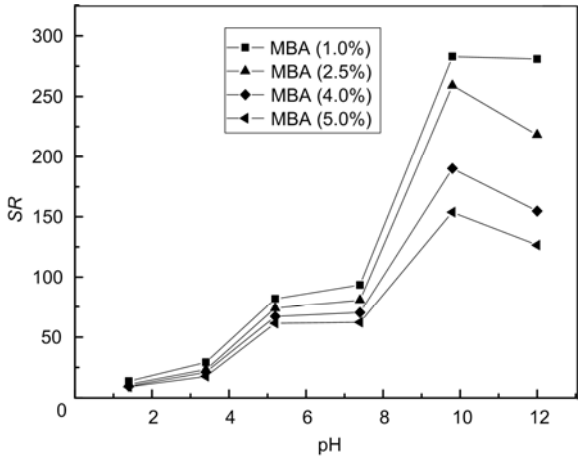

Fig.4 The *SR* of the PAA hydrogels prepared with various contents of crosslinking agent as a function of pH.

When the hydrogels are immersed in buffer solutions with low pH (pH < 4), the ionization of the carboxylic acid groups is very low, and the electrostatic repulsion between the ionized groups in the networks has hardly any contribution to the swelling of the hydrogels. This leads to a collapsed polymer network with a rather limited *SR*. A transition of the *SR* can be observed between pH 4 and pH 5 owing to the pK_a of the PAA. At this pH range, dissociation of the carboxylic acid groups occurs during the Na_2HPO_4 treatment. Both the charge repulsion and the presence of free counter-ions in the gel, which cause a high osmotic pressure, contribute to the improved *SR*. The pK_a of the AAc is reported in the literature.[12] At higher pH (5.2－7.4), the *SR* of the hydrogels is almost constant

because of the charge repulsion and elastic stress of the hydrogel networks. In alkaline buffer solutions (pH $\leqslant$ 9.8), the carboxylic acid groups become progressively ionized. Therefore, the hydrogels swell more rapidly because of a large swelling force created by the electrostatic repulsion between the ionized groups in the network. At pH > 9.8, the higher concentration of Na^+ will restrain the extending of the hydrogel networks, therefore the swelling of the hydrogels is inhibited.

Fig.5 shows the effect of pH on the *SR* of the hydrogels prepared at various dose rates of irradiation. It can be found that the *SR* of the hydrogels is greatly influenced by the dose rate. At pH values of more than 4, the *SR* of the hydrogels increases with an increase in the dose rate. This can be explained as follows: the lower dose rate means longer irradiation time, which consequently prolongs the propagation of the polymerization process, leading to a higher degree of crosslinking. Figs.4 and 5 are in very good accordance when showing the effect of pH on the *SR* of the PAA hydrogels.

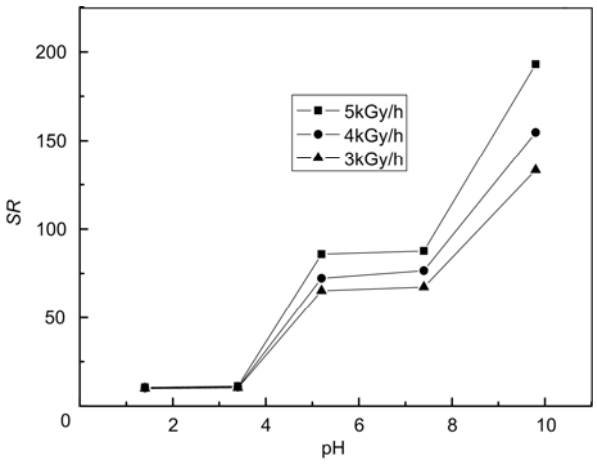

Fig.5 The *SR* of the PAA hydrogels prepared at different dose rates as a function of pH.

4 Conclusions

The pH-sensitive PAA hydrogels were prepared by gamma-ray irradiation with an absorbed dose from 14 kGy to 22 kGy. The influences of dose, monomer concentration, cross-linking agent content, ionic strength, and pH of the swelling medium on the *SR* of these hydrogels were investigated in detail. The results show that the *SR* of the hydrogels decreases with the increase of the absorbed dose, the monomer concentration and the cross-linking agent content. These hydrogels indicate the proper pH-sensitive characteristics. The *SR* of the hydrogels in alkaline solution is much higher than that in acid solution. Also, the ionic strength can influence the *SR* of the hydrogels. The more the concentration is, the less the *SR* is.

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